Rate Coefficients for the Reactions of Cl Atoms with a Series of C_3-C_6 Hydroxyalkyl Nitrates at 296 ± 2 K

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Rate coefficients for the gas-phase reactions of chlorine atoms with a series of C_3-C_6 hydroxyalkyl nitrates of atmospheric interest have been determined at 296 ± 2 K and atmospheric pressure. The experiments were conducted using the relative rate technique combined with solid-phase microextraction (SPME) sampling followed by gas chromatography (GC) analysis with an electron capture detector (ECD). The experiments were performed in a collapsible 100 L PVF-film (Tedlar) reaction chamber. It is shown that the presence of the hydroxy group enhances the reactivity of the hydroxyalkyl nitrates toward the Cl atom as compared to the corresponding alkyl nitrates and alkyl dinitrates. The Cl atom reactivity toward the hydroxyalkyl nitrates increases with the length of the alkyl chain and with increasing separation between the hydroxy and the nitrooxy groups. Tropospheric lifetimes are calculated using the determined rate coefficients and the atmospheric implications are briefly discussed.

Introduction

Organic nitrates are reservoir species for reactive nitrogen oxides. They form during the atmospheric photodegradation of hydrocarbons in the presence of nitrogen oxides. This process competes with the chemical cycle leading to ozone production since it sequesters both nitrogen oxides and organic radicals.[1−4]

A common class of bifunctional organic nitrates are the hydroxyalkyl nitrates that form in the atmospheric photodegradation of alkanes and alkenes. Several pathways for their formation exist. β-Hydroxyalkyl nitrates form in the oxidation of alkenes by OH radicals.[5,6] δ-Hydroxyalkyl nitrates result from a 1,5-H shift of alkoxy radicals following the reactions of the OH radical with long chain (≥4) alkanes.[7−10] Pathways leading to the formation of γ-Hydroxyalkyl nitrates in the atmosphere are not well-known. However, it was recently proposed that NO_3 reactions with unsaturated alcohols such as 2-methyl-3-buten-2-ol could form various products including an organic nitrate with the hydroxy and nitrooxy groups in a γ position.[11] Although organic nitrate formation yield is small for short *n*-alkanes,[12] the high emission flux of their precursors in the urban atmosphere may lead to significant production of the corresponding nitrates.

Hydroxyalkyl nitrates have been measured in the atmosphere; C_2-C_4 β-hydroxyalkyl nitrates were identified and estimated to account for ∼15% of the total atmospheric organic nitrates.[13,14] C_3-C_5 β-hydroxyalkyl nitrates in the low ppt range have been measured in marine air[15] at about 10% of their urban concentrations.[13,14] To our knowledge, γ- and δ-hydroxyalkyl nitrates have not yet been identified in atmospheric samples, mainly due to the lack of appropriate standards.

Atomic chlorine is generated by photolysis of molecular chlorine released to the atmosphere via reactions in sea salt particles and contributes to oxidation of organic compounds in the marine boundary layer.[16] Peak concentrations of atomic chlorine as high as 10^4-10^5 cm^{-3} in the marine boundary layer in the early morning hours have been predicted.[17−19] The concentration of Cl atoms in the global troposphere is lower and is estimated to be 10^2-10^5 cm^{-3}.[16,19−21] Considering that Cl rate coefficients are often a factor of 10 higher than the corresponding OH rate coefficients, it is possible that the reactions with Cl atoms may play a significant role in the degradation of organic compounds in urban coastal air. A detailed understanding of the atmospheric chemistry of hydroxyalkyl nitrates is needed for accurate assessment of their environmental impact. For this, kinetic and mechanistic data concerning the reaction of Cl atoms is needed. The kinetics of the reactions of chlorine atoms with alkyl nitrates have been studied by several researchers.[22,23] However, to the best of our knowledge, the reactions of multifunctional organic nitrates, such as the hydroxyalkyl nitrates with atomic chlorine, have not yet been investigated.

The purpose of this study is to determine the rate coefficients for the gas-phase reactions of chlorine atoms with a series of hydroxyalkyl nitrates of atmospheric interest at atmospheric pressure and temperature of 296 ± 2 K and to understand the effect of the hydroxyalkyl nitrates structure on their reactivity. For this purpose, a relative rate technique was employed, combined with solid-phase microextraction (SPME) sampling and analysis by GC equipped with an electron capture detector (ECD). The SPME technique offers many advantages for such kinetic measurements since it is fast, sensitive, selective, solvent-free, easy to use, and inexpensive.[24,25] This method has only recently been applied to gas-phase kinetic studies.[26,27]

Principles of the Relative Rate Technique. Cl atom rate coefficients were determined using a relative rate technique, which has been extensively described in the literature.[12,28,29] Briefly, the underlying principle of this method is to measure the decay rate of the selected hydroxyalkyl nitrate (HN) relative to a reference compound (R), whose Cl atom reaction rate coefficient is known.

In the presence of atomic chlorine, the reactant hydroxyalkyl nitrate and the reference compound decay via reactions 1 and 2:

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$$\mathrm{HN} + \mathrm{Cl} \xrightarrow{k_{\mathrm{HN}}} \text{products} \tag{1}$$

$$\mathrm{R} + \mathrm{Cl} \xrightarrow{k_{\mathrm{R}}} \text{products} \tag{2}$$

where k_{HN} and k_R are the rate coefficients for reactions 1 and 2, respectively. Provided that both reactants are removed solely by the reaction with Cl atoms and that they do not re-form in the reaction chamber (see validation section), the following relation is obtained:

$$\ln\left(\frac{[\mathrm{HN}]_0}{[\mathrm{HN}]_t}\right) = \left(\frac{k_{\mathrm{HN}}}{k_{\mathrm{R}}}\right) \ln\left(\frac{[\mathrm{R}]_0}{[\mathrm{R}]_t}\right) \tag{I}$$

where $[HN]_0$ and $[R]_0$ and $[HN]_t$ and $[R]_t$ 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 $\ln([R]_0/[R]_t)$ 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_R, the value of k_{HN} may be calculated.

Experimental Section

1. Chemicals and Materials. The kinetic experiments were conducted with 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, 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 nitrates (reference compounds):* 1-butyl nitrate and 1-pentyl nitrate. (For simplicity, the nomenclature introduced by Schneider and Ballschmiter[30] for nitrates will be used in this paper: $1OH2C_3$, $2OH1C_3$, $1OH2C_4$, $2OH1C_4$, $1OH3C_4$, $2OH4C_4$, $1OH4C_4$, $1OH2C_5$, $2OH1C_5$, $1OH4C_5$, $2OH5C_5$, $1OH6C_6$, $1,4C_4$, $1C_4$, and $1C_5$, respectively). For clarification, Figure 1 shows the hydroxyalkyl nitrates and the alkyl dinitrate studied and their shorthand notation.

The hydroxyalkyl nitrates (except $1OH6C_6$) were all synthesized by selective nitration of the parent diols or epoxides. They were purified (>98%) and characterized according to the previously developed procedures.[31−33]

$1OH6C_6$ was synthesized, for the first time, by a new procedure: nitration of (iodobutoxy)-*tert*-butyldimethylsilane by silver nitrate. The 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 (the detailed procedure, for the preparation of $1OH4C_4$, is described in the Appendix). This synthesis method is very specific, results in high yields, is less complicated, and demands less purification stages as compared to our previously published synthesis methods.[32] Although the procedure described here was used for the preparation of $1OHnC_n$ hydroxyalkyl nitrates, other silane reactants may be chosen for producing the corresponding hydroxyalkyl nitrates.

1,4-Butyl dinitrate and alkyl nitrates were prepared via nitration of the parent 1,4-butanediol and *n*-alcohol, respectively, by fuming HNO_3 and H_2SO_4 in dichloromethane.[34]

The diluent gas used in the kinetic experiments was synthetic air (>99.999%). Nitrogen (>99.999%) was also used, but since no difference was observed between the experiments conducted with either synthetic air or nitrogen, synthetic air was chosen as the bath gas. Molecular chlorine (99.999%) was used without any further purification.

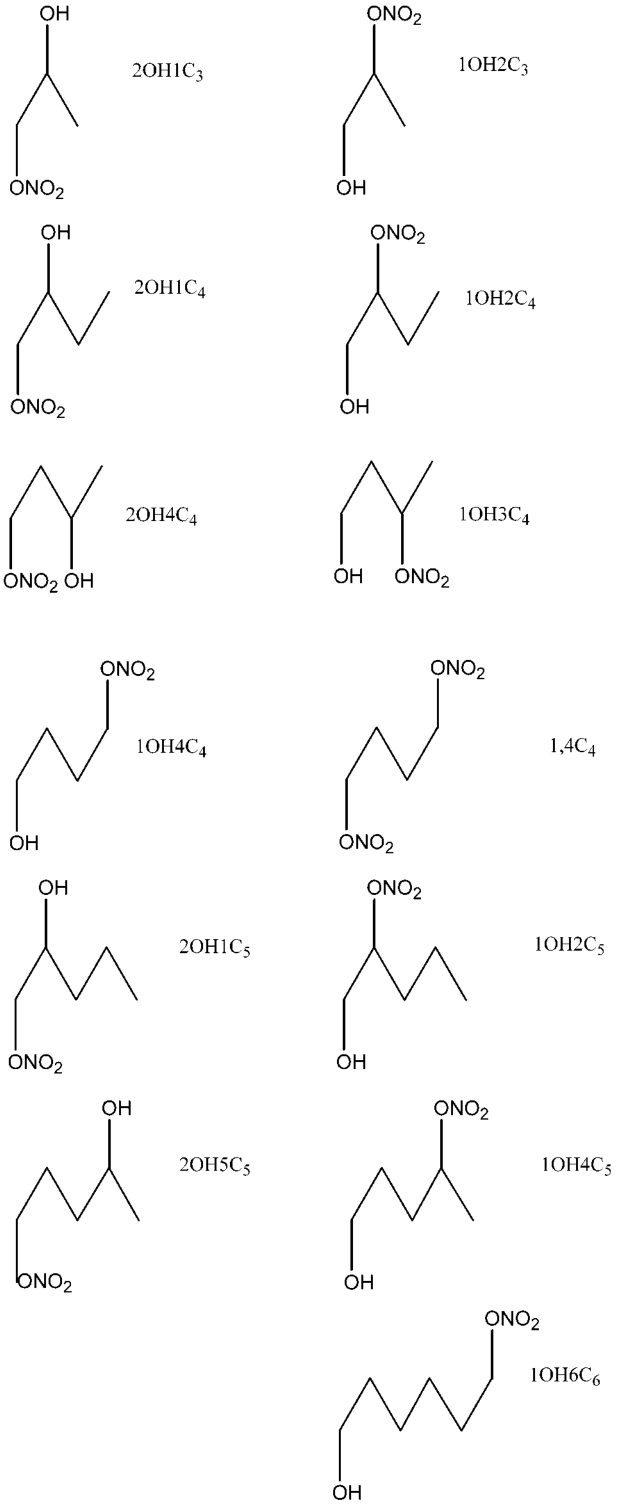

Figure 1. Structure of the studied compounds and their shorthand notation.

The SPME fiber used for sampling all the nitrates was Stableflex poly(dimethylsiloxane)/divinylbenzene, PDMS/DVB, 65 μm coating thickness.[35] The fibers were conditioned inside the GC injector port for 30 min at 260 °C before use.

2. Reference Compounds. Alkyl nitrates, 1-pentyl nitrate and 1-butyl nitrate, were chosen as reference compounds since they have known reaction rate coefficients toward Cl atoms, which are within a factor of 10 of the predicted hydroxyalkyl nitrate rate coefficients. The rate coefficients of 1-pentyl nitrate and 1-butyl nitrate at 296 K are $k_{Cl} = 1.57 \times 10^{-10}$ and $k_{Cl} = 9.24 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively.[23,22] It was verified that these alkyl nitrates do not photolyze or stick to the walls of the reaction chamber. No chromatographic interference between the retention times of these alkyl nitrates and the hydroxyalkyl nitrates was observed under the conditions employed.

3. Experimental Procedure. Kinetic experiments were carried out at 296 ± 2 K and at atmospheric pressure using a collapsible 100 L PVF-film (Tedlar) reaction chamber (SKC Inc.). The reaction chamber was equipped with three inlets positioned at its upper, central, and lower sections. The reaction chamber was homogeneously surrounded by 20 UV fluorescent lamps (Philips TL 40W/05, $300 \leq \lambda \geq 460$ 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.

Desired amounts of the hydroxyalkyl nitrate and the reference compounds were prepared off-line in a separate vacuum system: known amounts were injected as liquids through a septum into evacuated Pyrex bulbs. Molecular chlorine was introduced into another evacuated Pyrex bulb. The bulbs were then connected one after the other to the reaction chamber, at the upper and lower inlets, alternatively, to ensure good mixing, and 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 reaction chamber were left to homogenize for ~30 min, prior to irradiation. During that time, the chamber was kept in the dark to avoid photolysis of the molecular chlorine. After stabilizing, the reaction chamber was irradiated for short periods (usually 30 s to 2 min). Between each irradiation period, two SPME samples were taken.

Chlorine atoms were generated directly by the photolysis of molecular chlorine:

$$Cl_2 + h\nu(300 \leq \lambda \leq 460 \text{ nm}) \rightarrow 2Cl \qquad (3)$$

The typical initial concentrations of the reactant mixture were $(2-6) \times 10^{13}$ molecule cm^{-3} for hydroxyalkyl nitrates and alkyl dinitrate, $(4-8) \times 10^{12}$ molecule cm^{-3} for alkyl nitrate reference compounds, and $(1-2) \times 10^{14}$ molecule cm^{-3} for molecular chlorine.

After each experiment, the reaction chamber was pumped and cleaned out by filling it with nitrogen (>99.999%). The pumping and filling cycle was repeated several times until the nitrates were not detected.

4. Analytical Procedure. The decay of the organic nitrates due to reaction with atomic chlorine 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 overlapping of the other reactants nor products present in the reaction chamber.

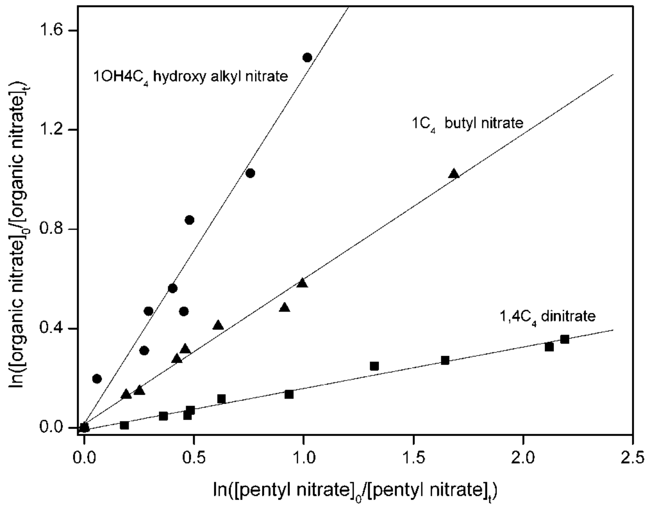

Figure 2. Relative rate plots for chlorine atoms experiments at 1 atm pressure and 296 ± 2 K of 1OH4C$_4$, 1,4C$_4$, and 1C$_4$. Pentyl nitrate is used as the reference compound.

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 the case of saturation of the detector response. The retention times were the same for the direct liquid and the SPME injections.

The gas-phase sampling using SPME allows for simultaneous sampling of both the hydroxyalkyl nitrates and the reference compounds. 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. After sampling, the fiber was inserted into the GC injector for 30 s for thermal desorption, followed by chromatographic separation and quantification. 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.

Results

The data obtained from the SPME samplings was plotted in accordance with eq I. Relative rate plots for 1,4C$_4$, 1OH4C$_4$, and 1C$_4$ are shown in Figure 2, and for 1OH6C$_6$, and 2OH5C$_5$ are shown in Figure 3 (both figures use pentyl nitrate (1C$_5$) as a reference compound). The slopes of the plots were obtained by least-squares fit. In all cases, the least-squares intercepts of the plots were within two standard deviations of zero. The linear correlation coefficients (r) were always better than 0.98 for all compounds. Each data point on the curves represents inaccuracy of ~10−20%. These errors are associated with the measurements and result mainly from the manual SPME procedure (e.g., imprecise sampling time periods, manual injections into the GC) and reactant preparation (syringe liquid injection to the Pyrex bulb, vacuum line dilution, pressure measurements, etc.).

The slopes of the relative rate plots have been placed on an absolute basis using the following rate coefficients for the reference compounds: $k_{Cl} = (9.24 \pm 0.2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for 1-butyl nitrate; $k_{Cl} = (1.57 \pm 0.03) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for 1-pentyl nitrate.[22] The resulting rate coefficients of the hydroxyalkyl nitrates 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, and alcohols.[22,29,36−38] The errors quoted in

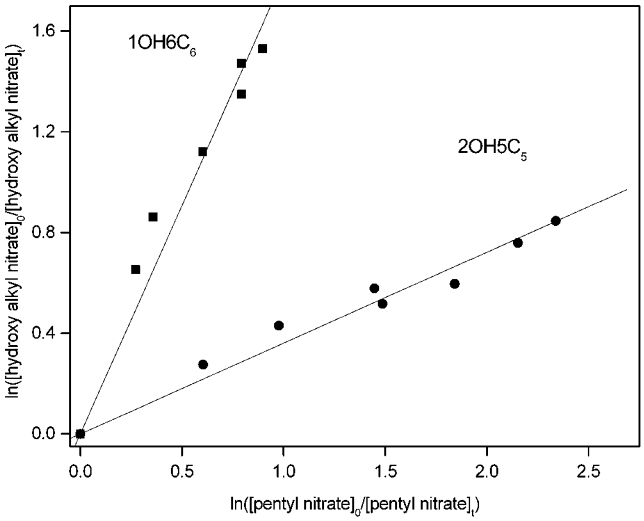

Figure 3. Relative rate plots for chlorine atoms experiments at 1 atm pressure and 296 ± 2 K of $1OH6C_6$ and $2OH5C_5$. Pentyl nitrate is used as the reference compound.

TABLE 1: Rate Coefficients (95% Confidence Level) and Tropospheric Lifetimes for the Reactions of Cl Atoms with C_3−C_6 Hydroxyalkyl Nitrates, Alkyl Nitrates, and Alkyl Dinitrate at 296 ± 2 K and Atmospheric Pressure

compound[a]	k_{Cl} ($\times 10^{-10}$)[b] (cm^3 molecule^{-1} s^{-1})	ref compound[c]	atmospheric lifetime (days)[d]
$1OH2C_3$	0.42 ± 0.08	$1C_4$	5.5
$2OH1C_3$	0.45 ± 0.09	$1C_4$	5.1
$1OH2C_4$	0.98 ± 0.10	$1C_4$; $1C_5$	2.4
$2OH1C_4$	0.87 ± 0.09	$1C_4$; $1C_5$	2.7
$1OH3C_4$	1.39 ± 0.26	$1C_4$; $1C_5$	1.7
$2OH4C_4$	1.40 ± 0.16	$1C_4$; $1C_5$	1.7
$1OH4C_4$	1.82 ± 0.36	$1C_4$; $1C_5$	1.3
$1OH2C_5$	1.59 ± 0.16	$1C_4$; $1C_5$	1.5
$2OH1C_5$	1.25 ± 0.19	$1C_4$; $1C_5$	1.9
$1OH4C_5$	1.56 ± 0.31	$1C_4$; $1C_5$	1.5
$2OH5C_5$	2.05 ± 0.22	$1C_4$; $1C_5$	1.1
$1OH6C_6$	2.44 ± 0.26	$1C_4$; $1C_5$	0.9
$1C_4$	0.92 ± 0.09	$1C_5$	2.5
$1C_5$	1.57 ± 0.16	$1C_4$	1.5
$1,4C_4$	0.39 ± 0.08	$1C_4$; $1C_5$	5.9

[a] For simplicity, the nomenclature introduced by Schneider and Ballschmiter[30] for multifunctional nitrates is used in the table. [b] The rate coefficients, k_{Cl}, are calculated according to eq I. [c] Rate coefficients of the reference compounds: $k_{1C4} = 9.24 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}; $k_{1C5} = 1.57 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}.[22] [d] Tropospheric lifetimes for hydroxyalkyl nitrates with respect to removal by Cl atoms were calculated using the relationship: $\tau = (k_{Cl}[Cl]\}^{-1}$ and assuming Cl concentration of 5×10^4 atom cm^{-3}.[17−21]

Table 1 reflect the accuracy of the measurements and include statistical uncertainties of the averaged values and an additional 10% uncertainty to account for uncertainties in the reference rate coefficients. The estimated overall errors of these rate constants are ~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 between the amount of reactants extracted by the SPME fiber and their initial concentrations in the reaction chamber was observed for all the studied compounds. The linearity between the chromatographic response and the concentrations of the compounds was confirmed over 3 orders of magnitude.

The reproducibility of the measurements was excellent: variation between repeated SPME samplings was found to be <10%. There were no variations in the rate coefficients obtained upon changing the initial concentrations of the reactants used, the diluent gas, the reference compound, the light intensity, or the photolysis time.

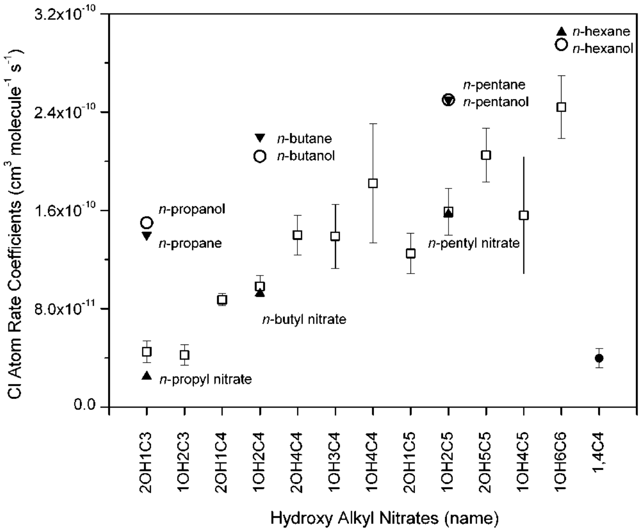

Figure 4. Schematic presentation of the Cl atom rate coefficients of the hydroxyalkyl nitrates and dinitrate and a comparison with their corresponding alkyl nitrates, alkanes, and alcohols: (□) hydroxyalkyl nitrates; (▼) *n*-alkanes; (▲) alkyl nitrates; (○) alcohols; (●) dinitrate.[22,29,36−38]

Discussion

1. Validation of the Experimental System, Procedure, and Measurements. The relative rate technique assumes that both the reactant and the reference compounds are removed solely by the reaction with chlorine atoms. A series of control experiments were performed to verify this assumption for each of the organic nitrates. Wall losses were confirmed to be unimportant by letting the reactants, reference compounds, and molecular chlorine stay in the reaction chamber for about 1 h and observing the same initial and final concentrations. In addition, mixtures of the reactant, reference, and molecular chlorine were allowed to stand in the dark for 2 h, to check for possible dark reactions. In all cases, no decay of the reactants or of the reference compounds was observed. In addition, mixtures of the organic nitrates were irradiated at maximum light intensity in the absence of molecular chlorine for a couple of hours. No decrease in their concentrations was observed. Thus, under the experimental conditions employed, the organic nitrates were photochemically stable.

Moreover, the very good linearity of the plots passing through the origin (shown in Figures 2 and 3) suggests that the secondary reactions are insignificant. Finally, no interference between the retention times of the reactants, reference, and oxidation products was observed for the gas chromatography conditions employed. The same rate coefficients were obtained from experiments using different reference compounds, implying that the results are independent of the reference compound.

To the best of our knowledge, this is the first study of the rate coefficients of Cl atom reactions with hydroxyalkyl nitrates and the C_4 dinitrate. Thus, a comparison to the literature is not available. Using two alkyl nitrate reference compounds in each experiment as an intercalibration experiment validated the results. The relative rate plots for the two reference compounds themselves were plotted one against the other, for each experiment, to give their relative loss rate. Their obtained rate coefficients were compared to the literature values and an excellent agreement was found between them (see Table 1).

The agreement between the values obtained here and those from the literature indicates that the experimental system and procedure are valid and can be used to determine Cl atom reaction rate coefficients with the various hydroxyalkyl nitrates and dinitrate. In addition, it implies that choosing one of the reference compoundss does not influence the results.

2. Cl Atom Rate Coefficients. This study provides a systematic investigation of the chlorine atoms reactions with a series of multifunctional compounds, the hydroxyalkyl nitrates. The reaction of the electrophilic Cl atoms with substituted alkanes is believed to proceed by H-atom abstraction process.[1,16] The Cl atom reactivity toward the hydroxyalkyl nitrates is observed to be closely related to their chemical structure. Two structural parameters determine the Cl atom reactivity toward hydroxyalkyl nitrates: the length of the hydrocarbon chain and the separation between the hydroxy and the nitrooxy groups.

The nitrooxy group significantly decreases the Cl atom reactivity relative to the corresponding unsubstituted alkanes. This behavior is attributed to its 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.[39] For example: k_{Cl} for butane is 2.2×10^{-10} cm^3 molecule^{-1} s^{-1},[37] whereas k_{Cl} for 1-butyl nitrate is 0.92×10^{-10} cm^3 molecule^{-1} s^{-1}.[22] k_{Cl} of pentane is 2.5×10^{-10} cm^3 molecule^{-1} s^{-1},[29] whereas k_{Cl} of pentyl nitrate is 1.57×10^{-10} cm^3 molecule^{-1} s^{-1} [22] (see Figure 4). The presence of the nitrooxy group decreases the Cl atom reactivity of the hydroxyalkyl nitrate as compared to the corresponding alcohols. For example: k_{Cl} for propanol is 1.5×10^{-10} cm^3 molecule^{-1} s^{-1},[36] whereas k_{Cl} for C$_3$ hydroxyalkyl nitrate is 0.45×10^{-10} cm^3 molecule^{-1} s^{-1} (see Table 1 and Figure 4) and k_{Cl} for butanol is 2.04×10^{-10} cm^3 molecule^{-1} s^{-1},[36] and k_{Cl} for the most reactive C$_4$ hydroxyalkyl nitrate is 1.82×10^{-10} cm^3 molecule^{-1} s^{-1} (see Table 1 and Figure 4).

The presence of the hydroxy group, on the other hand, is expected to somewhat enhance the Cl atom reactivity as compared to the corresponding alkyl nitrates and dinitrates. This is indeed observed, as is demonstrated in Figure 4, and is similar to the trend observed for reactions of Cl atoms with alcohols. Nelson et. al.[36] observed that alcohols are more reactive than the corresponding alkanes due to lowering of the C$-$H bond dissociation energies for carbon bound to a hydroxy group by about 4$-$5 kcal mol^{-1}, thus facilitating the hydrogen abstraction.[36] This trend is similar to the trend observed also for reactions of hydroxy radical with small alcohols, which is also explained by the more labile α-hydrogen atom to the OH group. However, since most of the reaction proceeds via H atom abstraction from the C$-$H bond, the effect for alcohols is not expected to be significant for larger alcohols.[36,40]

There is little difference between the Cl atom reactivity toward the two isomers (for example: 1OH2C$_4$ and 2OH1C$_4$) of the hydroxyalkyl nitrates.

As shown in Table 1 and Figure 4, for a constant separation between the hydroxy and the nitrooxy groups, there is an increase in the Cl atom reactivity with the increase in the alkyl chain length. Addition of the CH$_2$ group enhances the overall reactivity toward Cl atoms because of its high reactivity in the central position of the molecule. This results from the lowering of the C$-$H bond dissociation energies. Hence, the Cl atom reactivity toward β-hydroxyalkyl nitrates decreases in the order C$_5$ β-hydroxyalkyl nitrate (1OH2C$_5$; 2OH1C$_5$) > C$_4$ β-hydroxyalkyl nitrate (1OH2C$_4$; 2OH1C$_4$) > C$_3$ β-hydroxyalkyl nitrate (1OH2C$_3$; 2OH1C$_3$). For δ-hydroxyalkyl nitrates, the Cl atom reactivity toward 2OH5C$_5$ is higher than that toward 1OH4C$_4$, since the former has a longer alkyl chain.

The Cl atom reactivity toward hydroxyalkyl nitrates with the same chain length increases as the separation between the hydroxy and the nitrooxy group increases. This is probably because the hydroxy group better enhances the Cl atom reactivity and the effect of the nitrooxy group diminishes with increasing distance. Therefore, the Cl atom reactivity toward C$_4$ hydroxyalkyl nitrate decreases in the order δ-hydroxy nitrate (1OH4C$_4$) > γ-hydroxy nitrate (1OH3C$_4$; 2OH4C$_4$) > β-hydroxy nitrate (1OH2C$_4$; 2OH1C$_4$). 1OH6C$_6$ is the longest hydroxyalkyl nitrate and exhibits the largest separation between the two functional groups. Thus, its Cl atom rate coefficient is the highest (see Figure 3 and Table 1).

As can be seen in Figure 2 and Table 1, within the C$_4$ organic nitrates, the Cl atom reactivity toward 1,4C$_4$ dinitrate is the lowest due to the presence of the two nitrooxy groups. It is ~4 times lower than the Cl atom reactivity toward the corresponding 1OH4C$_4$ hydroxyalkyl nitrates, and ~2 times lower than the Cl atom reactivity toward the 1C$_4$ alkyl nitrate.

To summarize, atomic chlorine is highly reactive toward the hydroxyalkyl nitrates. The differences between the rate coefficients for the Cl atom reaction with the various hydroxyalkyl nitrates are not very large. This reaction probability is high almost regardless of the collision site, and the chemical structure plays a limited role in determining the reaction rate coefficients.

3. Atmospheric Implications. The atmospheric lifetime of hydroxyalkyl nitrates, with respect to removal by reaction with Cl atoms, can be calculated from the measured rate coefficients. Table 1 presents the tropospheric lifetimes of hydroxyalkyl nitrates toward reactions with Cl atoms estimated by assuming a Cl concentration of 5×10^4 atom cm^{-3} in the marine boundary layer.[17−21] The estimated lifetimes of the hydroxyalkyl nitrates are in the range of 0.9 days for 1OH6C$_6$ to 5.5 days for 1OH2C$_3$. The C$_4$$-C_5$ alkyl nitrate and C$_4$ dinitrate atmospheric lifetimes are in the range of those of the hydroxyalkyl nitrates, with the latter exhibiting the longest lifetime of 5.9 days.

These estimates suggest that in the marine boundary layer, at peak concentration of Cl atoms, gas-phase reactions of hydroxyalkyl nitrates (C$_3$$-C_5$ β-hydroxyalkyl nitrates in the low ppt range have been measured in marine air[15]) with Cl atoms may be a significant loss process. This is especially relevant for the larger hydroxyalkyl nitrates and should be taken into account in addition to their other loss mechanisms. Organic nitrates are long-lived and can undergo long-range transport to remote areas.[6,32] Thus, hydroxyalkyl nitrates, which mainly form in an urban atmosphere, may be transported toward coastal regions and interact with marine air masses that can have significant Cl atoms concentrations. Alternatively, gas-phase reactions of hydroxyalkyl nitrates with Cl atoms may be a significant loss process for hydroxyalkyl nitrates produced directly in urban coastal regions. Since the global tropospheric concentration of Cl atoms is much lower than within the marine boundary layer (~10^2 to 10^5 atom cm^{-3} [16,19−21]), the reaction of hydroxyalkyl nitrates with Cl atoms are probably not globally important (taking an average Cl concentration of ~10^3 atom cm^{-3} yields lifetimes in the range of 47 days for 1OH6C$_6$ to 276 days for 1OH2C$_3$). Even so, the rate coefficients presented here show that atomic chlorine is highly reactive with the hydroxyalkyl nitrates. Therefore, even a small Cl atom concentration can compete with the other main atmospheric loss process of the hydroxyalkyl nitrates such as gas-phase reactions with OH radicals, photolysis, partitioning into organic aerosols and wet deposition.[32,35]

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Appendix

1OH4C$_4$ Synthesis: Nitration of (4-Iodobutoxy)-*tert*-butyldimethylsilane by Silver Nitrate. In a 100 mL flask was dissolved 2.4 g of (4-iodobutoxy)-*tert*-butyldimethylsilane in 40 mL of extra dry acetonitrile. The solution was cooled to −10 °C using ethylene glycol/dry ice bath. Silver nitrate (2.6 g, 2 equiv) was added to the flask. After 5 min, the cooling bath was removed, and the solution was stirred at room temperature for 30−50 min. The reaction was monitored by TLC (eluents: hexane, ethyl acetate/hexane 1:4).[32] Afterward, the reaction mixture was filtered from precipitated yellow AgI. A 4 mL aliquot of water was added to the filtrate and (4-nitrooxybutoxy)-*tert*-butyldimethylsilane was hydrolyzed for 40 min at room temperature. The reaction was monitored by TLC (eluents: hexane, ethyl acetate/hexane 1:1). Then the reaction mixture was filtered. Water and 40 mL of ethyl acetate were added to the reaction mixture, and as a result, two phases appeared and were separated by a separation funnel. The organic phase was further dried over $MgSO_4$, and organic solvents were evaporated under vacuum. The hydroxyalkyl nitrate residue from the organic phase was purified by flash chromatography on silica gel 60 (230−400 mesh) (eluent: ethyl acetate/hexane 1:1). The purity of the resulting hydroxyalkyl nitrates was confirmed by gas chromatography as well as IR, ^{1}H NMR, and ^{13}C NMR (>99%).

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