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Alkyl Nitrate, Hydroxyalkyl Nitrate, and Hydroxycarbonyl Formation from the NO_x−Air Photooxidations of C_5−C_8 *n*-Alkanes

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Products of the gas-phase reactions of OH radicals with the *n*-alkanes *n*-pentane through *n*-octane at 298 ± 2 K and atmospheric pressure of air have been investigated using gas chromatography with flame ionization detection (GC-FID), combined gas chromatography−mass spectrometry (GC-MS), and in situ atmospheric pressure ionization tandem mass spectrometry. The formation yields of alkyl nitrates from *n*-hexane, *n*-heptane, and *n*-octane were measured by GC-FID, with the sum of the isomeric alkyl nitrates being 0.141 ± 0.020, 0.178 ± 0.024, and 0.226 ± 0.032, respectively. These alkyl nitrate yields are ~35% lower than previous data reported from this laboratory in the early 1980s. Using negative ion atmospheric pressure chemical ionization with the addition of pentafluorobenzyl alcohol to study the *n*-pentane through *n*-octane reactions and those of the fully deuterated *n*-alkanes, hydroxyalkyl nitrate products were identified from the *n*-pentane, *n*-heptane, and *n*-octane reactions for the first time and the presence of hydroxycarbonyl products was confirmed. Adding NO_2 to the chamber reaction mixture postreaction to form $[NO_2{\cdot}M]^-$ adducts of the hydroxycarbonyls and hydroxynitrates, together with the use of 5-hydroxy-2-pentanone and 2-nitrooxy-3-butanol as internal standards for the hydroxycarbonyls and hydroxynitrates, respectively, enabled the yields of the hydroxycarbonyl and hydroxynitrate reaction products to be estimated.

Introduction

In the troposphere, alkanes present in the gas phase react mainly with the OH radical[1] to form an alkyl radical.

$$\mathrm{OH + RH \rightarrow H_2O + \dot{R}} \qquad (1)$$

Alkyl radicals react rapidly with O_2 in the troposphere to form alkyl peroxy ($R\dot{O}_2$) radicals, which then react with NO, NO_2, HO_2 radicals or with other organic peroxy ($\acute{R}\dot{O}_2$) radicals.[1]

$$\mathrm{\dot{R} + O_2 \rightarrow R\dot{O}_2} \qquad (2)$$

$$\mathrm{R\dot{O}_2 + NO \rightarrow RONO_2} \qquad (3a)$$

$$\mathrm{R\dot{O}_2 + NO \rightarrow R\dot{O} + NO_2} \qquad (3b)$$

$$\mathrm{R\dot{O}_2 + NO_2 \rightleftarrows ROONO_2} \qquad (4)$$

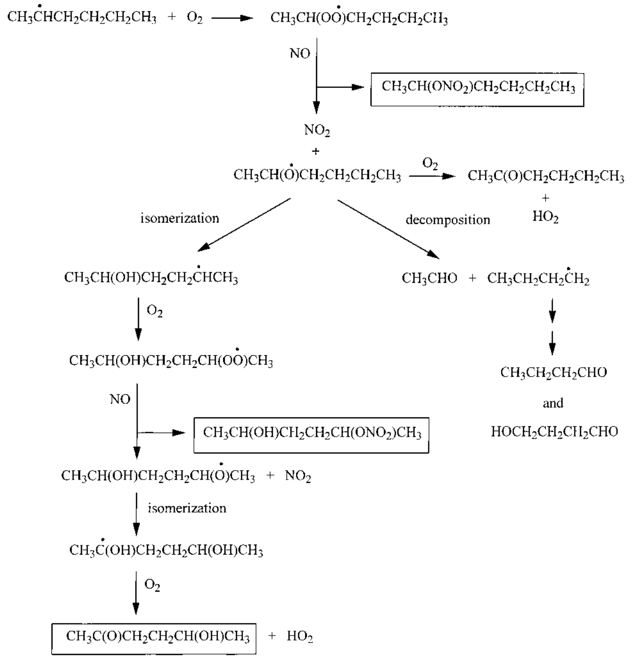
$$\mathrm{R\dot{O}_2 + HO_2 \rightarrow ROOH + O_2} \qquad (5)$$

$$\mathrm{R\dot{O}_2 + R\dot{O}_2 \rightarrow \alpha\ carbonyl + (1 - \alpha)\ alcohol + \acute{R}\dot{O}_2\ products + O_2} \qquad (6a)$$

$$\mathrm{R\dot{O}_2 + \acute{R}\dot{O}_2 \rightarrow R\dot{O} + \acute{R}\dot{O} + O_2} \qquad (6b)$$

In the presence of NO concentrations ≥10−30 parts-per-trillion, peroxy radical reactions with NO [reaction 3] will dominate[2] and the products of the alkyl peroxy radical reactions with NO are the corresponding alkoxy radical plus NO_2 or the alkyl nitrate, $RONO_2$,[1] as illustrated in Scheme 1 for the 2-hexyl radical formed from *n*-hexane.

SCHEME 1



The alkoxy radicals formed in reactions 3b and 6b then react with O_2, decompose by C−C bond scission, or isomerize through a six-membered ring transition state,[1] as shown in Scheme 1. The isomerization reaction becomes important for $\geq C_4$ alkanes and isomerization followed by O_2 addition to the 1,4-hydroxyalkyl radical results in the formation of a 1,4-hydroxyalkyl peroxy radical (Scheme 1). 1,4-Hydroxyalkyl peroxy radicals then react with NO, as shown in reactions 3a

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and 3b and Scheme 1, leading to the formation of a 1,4-hydroxyalkoxy radical plus NO_2 or a 1,4-hydroxyalkyl nitrate (note that the products analyzed in this work are denoted by boxes in Scheme 1). The 1,4-hydroxyalkoxy radical is expected to undergo a second (rapid) isomerization, leading to the formation of a 1,4-hydroxycarbonyl.[1] In addition to the formation of alkyl nitrates from reactions of the peroxy radicals with NO (as shown in reaction 3a and Scheme 1), reaction of the alkoxy radicals with NO_2 can also lead to alkyl nitrate formation.

$$R\dot{O} + NO_2 \rightarrow RONO_2 \tag{7}$$

The formation of alkyl nitrates from the OH radical-initiated reactions of C_2−C_8 *n*-alkanes and from a number of branched and cyclic alkanes has been studied previously.[3−13] For the *n*-alkanes, the alkyl nitrate yields were observed to increase monotonically with increasing carbon number in the *n*-alkane,[5] with molar yields ranging from ≤ 0.014 for ethane to 0.33 for *n*-octane at room temperature and atmospheric pressure of air.[5] The alkyl nitrate yields also increase with increasing pressure and with decreasing temperature.[6,8,9,14] To date, the formation of hydroxyalkyl nitrates from the OH radical-initiated reactions of alkanes, arising after alkoxy radical isomerization (Scheme 1), has been reported only from *n*-hexane.[15]

In this work, we have extended our recent study of the OH radical-initiated reaction of *n*-pentane,[10] using sampling, analysis, and calibration procedures which are significantly improved over those employed in our early 1980s studies,[5,6] to reinvestigate alkyl nitrate formation from the reactions of the OH radical with *n*-hexane through *n*-octane. In addition, we have used atmospheric pressure chemical ionization tandem mass spectrometry in the negative ion mode to investigate products of the *n*-pentane through *n*-octane and *n*-pentane-d_{12} through *n*-octane-d_{18} reactions, with a goal of observing the formation of the hydroxyalkyl nitrates predicted to be formed after alkoxy radical isomerization[1,15] and quantifying hydroxyalkyl nitrate and hydroxycarbonyl[15,16] products.

Experimental Methods

Experiments were carried out at 298 ± 2 K and 740 Torr total pressure of air in a 7900 L Teflon chamber with analysis by gas chromatography with flame ionization detection (GC-FID) and combined gas chromatography−mass spectrometry (GC-MS), with irradiation provided by two parallel banks of blacklamps; and in a 7300 L Teflon chamber interfaced to a PE SCIEX API III MS/MS direct air sampling, atmospheric pressure ionization tandem mass spectrometer (API-MS), again with irradiation provided by two parallel banks of blacklamps. Both chambers are fitted with Teflon-coated fans to ensure rapid mixing of reactants during their introduction into the chamber.

Hydroxyl radicals were generated by the photolysis of methyl nitrite in air at wavelengths >300 nm,[17] and NO was added to the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals.[17]

Teflon Chamber with Analysis by GC-FID. For the OH radical reactions carried out in the 7900 L Teflon chamber (at ∼5% relative humidity), the initial reactant concentrations (in molecule cm^{-3} units) were CH_3ONO, $(2.2−2.5) \times 10^{14}$; NO, $(2.2−2.3) \times 10^{14}$; and *n*-alkane, $(2.34−2.51) \times 10^{13}$. Irradiations were carried out at 20% of the maximum light intensity for 10−45 min, resulting in up to 37%, 43%, and 49% reaction of the initially present *n*-hexane, *n*-heptane, and *n*-octane, respectively. The concentrations of the *n*-alkane and alkyl nitrates were measured during the experiments by GC-FID. Gas samples of 100 cm^3 volume were collected from the chamber onto Tenax-TA solid adsorbent, with subsequent thermal desorption at ∼225 °C onto a DB-1701 megabore column in a Hewlett-Packard (HP) 5710 GC, initially held at 0 °C and then temperature programmed to 200 °C at 8 °C min^{-1}. In addition, gas samples were collected onto Tenax-TA solid adsorbent for GC-MS analyses, with thermal desorption onto a 60 m HP-5 fused silica capillary column in an HP 5890 GC interfaced to a HP 5970 mass selective detector operating in the scanning mode. GC-FID response factors were determined as described previously.[18] The alkyl nitrate standards contained the other secondary alkyl nitrates as impurities. The GC-FID calibrations, therefore, were based on summing the areas of the alkyl nitrate isomers and assuming identical GC-FID response factors for each alkyl nitrate. The molar GC-FID responses of the hexyl, heptyl, and octyl nitrates were consistent with their expected Equivalent Carbon Numbers,[19] verifying that wall losses in these calibrations were minor or negligible, in contrast to what is now suspected for our previous study.[5] The unique MS fragmentation patterns of the alkyl nitrates allowed the various isomers to be distinguished from one another. NO and initial NO_2 concentrations were measured using a Thermo Environmental Instruments, Inc., Model 42 NO−NO_2−NO_x chemiluminescence analyzer.

Teflon Chamber with Analysis by API-MS. In the experiments with API-MS analyses, the chamber contents were sampled through a 25 mm diameter × 75 cm length Pyrex tube at ∼20 L min^{-1} directly into the API mass spectrometer source. The operation of the API-MS in the MS (scanning) and MS/MS [with collision-activated dissociation (CAD)] modes has been described elsewhere.[11,16] Use of the MS/MS mode with CAD allows the “product ion” or “precursor ion” spectrum of a given ion peak observed in the MS scanning mode to be obtained.[11]

The negative ion mode was used in these API-MS and API-MS/MS analyses, with negative ions being generated by the negative corona around the discharge needle. The superoxide ion (O_2^-), its hydrates $[O_2^-(H_2O)_n]$, and O_2 clusters $[O_2^-(O_2)_n]$ are the major reagent negative ions in the chamber diluent air.[20] Other reagent ions, for example, NO_2^- and NO_3^-, are then formed through reactions between the primary reagent ions and neutral molecules such as NO_2, and instrument tuning and operation were designed to induce cluster formation.[11,16] In one series of experiments, pentafluorobenzyl alcohol (PFBOH) was added by passing the sampled air stream from the chamber over a heated vial containing PFBOH (with PFBOH effusing through a pinhole in the cap of the vial).

Under the experimental conditions used, analytes were detected as adducts ions formed from reaction of the neutral analyte (M) and reagent ions such as O_2^-, NO_2^-, $[PFBOH{\cdot}O_2]^-$, and $[PFBOH{\cdot}NO_2]^-$ generated in the ion source region. For example,

$$O_2^- + M \rightarrow [O_2{\cdot}M]^-$$

$$NO_2^- + M \rightarrow [NO_2{\cdot}M]^-$$

$$[PFBOH{\cdot}O_2]^- + M \rightarrow [PFBOH{\cdot}O_2{\cdot}M]^-$$

$$[PFBOH{\cdot}NO_2]^- + M \rightarrow [PFBOH{\cdot}NO_2{\cdot}M]^-$$

where M can include PFBOH. Because of the presence of fluorine in the PFBOH-containing reagent ions, the PFBOH-containing dimers are detected with high sensitivity under negative ionization conditions and their higher masses allowed them to be readily distinguished from fragment ions. Ions are drawn by an electric potential from the ion source through the sampling orifice into the mass-analyzing first quadrupole or third quadrupole. Neutral molecules and particles are prevented from entering the orifice by a flow of high-purity nitrogen ("curtain" gas). The initial concentrations of CH_3ONO, NO, and *n*-alkane (or deuterated *n*-alkane) were $\sim(2.4-24) \times 10^{12}$ molecule cm^{-3} each, and irradiations were carried out at 100% of the maximum light intensity for 0.5−7.5 min or at 20% of the maximum light intensity for 2.5−10 min.

Chemicals. The chemicals used, and their stated purities, were as follows: *n*-heptane, Mallinckrodt; *n*-heptane-d_{16} (98%), *n*-hexane (99+%), 1-hydroxy-2-butanone (95%), 4-hydroxy-4-methyl-2-pentanone (99%), *n*-octane (99+%), pentafluorobenzyl alcohol (98%), and *n*-pentane (99+%), Aldrich Chemical Co.; *n*-hexane-d_{14} (99%), *n*-octane-d_{18} (99%), and *n*-pentane-d_{12} (98%), Cambridge Isotope Laboratories; 3-heptyl nitrate, 2-hexyl nitrate, and 3-octyl nitrate, Fluorochem, Inc.; 5-hydroxy-2-pentanone (96%), TCI America; and NO ($\geq$99.0% and *cis*-2-butene ($\geq$ 95%), Matheson Gas Products. Methyl nitrite was prepared and stored as described previously.[17]

Results and Discussion

GC-FID and GC-MS Analyses of Alkyl Nitrates. GC-MS analyses of irradiated $CH_3ONO/NO/n$-alkane/air mixtures showed the formation of 2- and 3-hexyl nitrate from *n*-hexane, 2-, 3-, and 4-heptyl nitrate from *n*-heptane, and 2-, 3-, and 4-octyl nitrate from *n*-octane, and the *n*-alkane reactants and the alkyl nitrate products were quantified by GC-FID. Because the alkyl nitrates also react with the OH radical, these secondary reactions were taken into account as described previously[5] using rate constants for reactions of the OH radical (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) of *n*-hexane, 5.45; *n*-heptane, 7.01; *n*-octane, 8.71; 2-hexyl nitrate, 3.06; 3-hexyl nitrate, 2.60; 2-hepyl nitrate, 4.67; 3-heptyl nitrate, 3.75; 4-heptyl nitrate, 3.56; 2-octyl nitrate, 6.03; 3-octyl nitrate, 5.11; and 4-octyl nitrate, 4.92. The rate constants for the *n*-alkanes at 298 K were those recommended by Atkinson,[1] those for 2- and 3-hexyl nitrate were those cited in Atkinson[21] and reevaluated using the recently recommended rate constant for the reference organic cyclohexane,[1] and those for the heptyl and octyl nitrates were calculated[22] using the group rate constants and group substituent factors given by Atkinson[22] and decreased by 3.6% to account for the recent reference organic recommendations of Atkinson.[1] The multiplicative correction factors F to take into account the secondary reactions of OH radicals with the alkyl nitrates increase with the rate constant ratio $k(OH + \text{alkyl nitrate})/k(OH + n\text{-alkane})$ and with the extent of reaction,[5] and were <1.15 for the hexyl nitrates, <1.22 for the heptyl nitrates, and <1.28 for the octyl nitrates. Figure 1 shows plots of the amounts of the 2-, 3-, and 4-heptyl nitrates, corrected for reaction with the OH radical, against the amounts of *n*-heptane reacted. Similar linear plots were observed for the *n*-hexane and *n*-octane reactions, and the alkyl nitrate formation yields (for the individual isomers as well as their sum) obtained by least-squares analyses of the data are given in Table 1, together with analogous formation yields from our study of the *n*-pentane reaction[10] using similar analysis procedures.

As noted above, in addition to alkyl nitrate formation from peroxy radical reactions with NO [reaction 3a], alkyl nitrates can also be formed from the combination reaction of alkoxy radicals with NO_2 [reaction 7]. The rate constant for reaction 7 is $\sim3.8 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} at room temperature.[1] The final NO concentrations in the experiments were $>1.0 \times 10^{14}$ molecule cm^{-3}, and with the expectation that ($[NO] + [NO_2]$) $\sim$ constant throughout the irradiations[23] then the maximum NO_2 concentrations were $<1.3 \times 10^{14}$ molecule cm^{-3}, corresponding to a reaction rate of alkoxy radicals due to reaction with NO_2 of $<5 \times 10^3$ s^{-1}. All of the alkoxy radicals formed from *n*-hexane, *n*-heptane, and *n*-octane can isomerize through a six-membered transition state,[1] with estimated isomerization rate constants at 298 K of $\sim2 \times 10^5$ s^{-1} for the 3-hexoxy radical, $\sim4 \times 10^5$ s^{-1} for the 4-heptoxy radical, and $\geq2 \times 10^6$ s^{-1} for the 2-hexoxy, 2- and 3-heptoxy, and 2-, 3-, and 4-octoxy radicals.[1] Based on these estimated rate constants for the competing isomerization reactions, formation of alkyl nitrates from reaction 7 could lead to a maximum formation yield of 3-hexyl nitrate and 4-heptyl nitrate of 0.025 and 0.012 (per 3-hexoxy or 4-heptoxy radical formed), respectively, and of the other alkyl nitrates measured of $\leq$0.0025 (per alkoxy radical formed). These alkyl nitrate formation yields from reaction 7 are much lower than the measured yields (per alkyl peroxy radical) of $\geq$0.14 (see Table 2) and are within the experimental uncertainties.

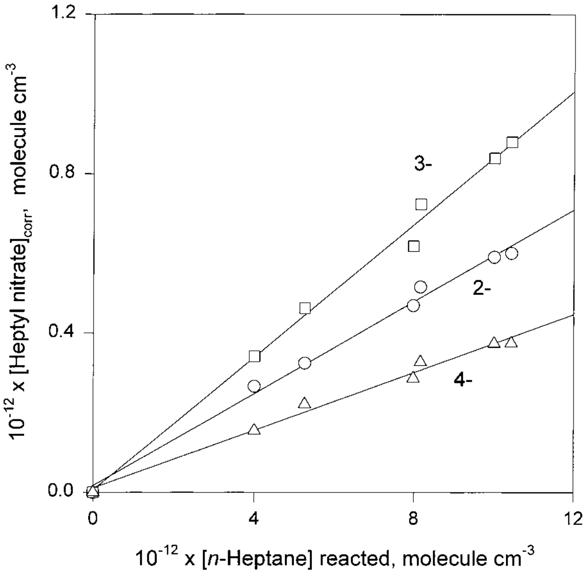

Figure 1. Plots of the amounts of 2-, 3-, and 4-heptyl nitrate formed, corrected for reaction with the OH radical (see text), against the amounts of *n*-heptane reacted with the OH radical in the presence of NO.

Our present alkyl nitrate yields (together with the pentyl nitrate yields from *n*-pentane[10]) are compared to our previous early 1980s data[5] in Table 1, showing that while our newer pentyl nitrates yield[10] is in agreement with the earlier data of Atkinson et al.,[5] our present alkyl nitrate yields from *n*-hexane, *n*-heptane, and *n*-octane are significantly lower than our previous data.[5] The previous measurements[5] were carried out in an $\sim$60 L Teflon reaction vessel with GC-FID analyses on a packed column, with 100 cm^3 samples being collected in a gastight all-glass syringe and concentrated by freezing out at liquid argon temperature prior to introduction onto the column via a gas sampling valve. Moreover, calibrations for the alkyl nitrates were carried out by introducing measured quantities of the liquids into a 46.5 L volume borosilicate glass vessel with replicate sampling and analysis. We now believe that this earlier study[5] had the potential for losses of the larger ($\geq C_6$) alkyl nitrates during the experiments, including (especially) during the alkyl nitrate calibrations, and that the data obtained[5] may have been subject to significant (and then unrecognized) uncertainties. Our present total heptyl nitrates yield of 0.178 ± 0.024 at 298 ± 2 K and 740 Torr total pressure of air is in good agreement with

TABLE 1: Formation Yields of Alkyl Nitrates from the OH Radical-Initiated Reactions of *n*-Hexane, *n*-Heptane, and *n*-Octane in the Presence of NO, at 298 ± 2 K and Atmospheric Pressure of Air[a]

				total nitrates[b]	
alkane	2-nitrate[a]	3-nitrate[a]	4-nitrate[a]	this work[a]	previous study[c]
ethane					<0.014
propane	0.029 ± 0.002[c]				0.036 ± 0.005
n-butane	0.073 ± 0.008[c]				0.077 ± 0.009
n-pentane	0.060 ± 0.010[d]	0.044 ± 0.006[d]		0.105 ± 0.014[d]	0.117 ± 0.013
n-hexane	0.059 ± 0.007	0.082 ± 0.010		0.141 ± 0.020	0.208 ± 0.027
n-heptane	0.059 ± 0.006	0.083 ± 0.009	0.036 ± 0.005	0.178 ± 0.024	0.293 ± 0.042
n-octane	0.062 ± 0.006	0.081 ± 0.008	0.083 ± 0.012	0.226 ± 0.032	0.318 ± 0.027

[a] Indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for the alkanes and alkyl nitrates of ±5% each. [b] From least-squares analyses of the sum of the nitrates. [c] From Atkinson et al.,[5] with the indicated errors being two least-squares standard deviations. [d] From Atkinson et al.;[10] see text.

TABLE 2: Formation Yields of Secondary Alkyl Nitrates from the Corresponding Secondary Alkyl Peroxy Radical in the OH Radical-Initiated Reactions of *n*-Hexane, *n*-Heptane, and *n*-Octane in the Presence of NO, at 298 ± 2 K and Atmospheric Pressure of Air

alkane	2-nitrate[a]	3-nitrate[a]	4-nitrate[a]	sec nitrates[c]	3-nitrate/2-nitrate[b]	4-nitrate/2-nitrate[b]
propane	0.039			0.039		
n-butane	0.084			0.084		
n-pentane[d]	0.106	0.126		0.115 ± 0.013	1.41 ± 0.08	
n-hexane	0.140	0.158		0.150 ± 0.019	1.40 ± 0.06	
n-heptane	0.177	0.202	0.175	0.187 ± 0.023	1.44 ± 0.11	1.26 ± 0.08
n-octane	0.224	0.238	0.243	0.235 ± 0.031	1.29 ± 0.08	1.32 ± 0.14

[a] Using the $-CH_3$ and $-CH_2-$ group rate constants and group substituent factors of Kwok and Atkinson[24] to calculate the fractions of the overall OH radical reaction proceeding by C−H abstraction at the individual carbon atoms. [b] From least-squares analyses of the 3-alkyl (or 4-alkyl) nitrate concentrations against those of the 2-alkyl nitrates (corrected for reactions with the OH radical). Indicated errors are two least-squares standard deviations. [c] From least-squares analyses of the sum of the nitrates, using the method of Kwok and Atkinson[24] to calculate the fraction of the overall OH radical reaction proceeding by C−H abstraction from secondary $-CH_2-$ groups. [d] From Atkinson et al.[10] (see text).

the total yield of heptyl nitrates measured by Harris and Kerr[9] at 730 Torr total pressure of air of 0.201 ± 0.041 at 298 K and 0.180 ± 0.015 at 299 K, although the heptyl nitrate isomer distribution reported by Harris and Kerr[9] differed significantly from our present and previous[5,6] heptyl nitrate isomer distributions. It should be noted that Harris and Kerr[9] quantified the heptyl nitrates by calibrating for 2-heptyl nitrate and assuming that the GC-electron capture detector responses of the isomeric heptyl nitrates were identical, while in the present work it is assumed that the GC-FID responses are identical.

Table 1 also contains the alkyl nitrate formation yields reported by Atkinson et al.[5] at room temperature and atmospheric pressure of air from the reactions of Cl atoms with ethane and the OH radical with propane and *n*-butane (all in the presence of NO). Combining these earlier data with the present work, the observed overall alkyl nitrate yields increase linearly with the carbon number of the *n*-alkane, with essentially zero ethyl nitrate formation from ethane and with an increase in the alkyl nitrate yield of 0.0354 ± 0.0026 per additional carbon atom in the *n*-alkane. As evident from the data presented in Table 1, only alkyl nitrates formed from the reactions of secondary alkyl peroxy radicals with NO were observed in our present study of *n*-hexane through *n*-octane, consistent with our previous data.[5,6] In the absence of direct experimental data, the estimation method of Kwok and Atkinson[24] for calculation of OH radical reaction rate constants can be used to calculate the rate constants for H-atom abstraction by the OH radical from the various $-CH_3$ and $-CH_2-$ groups in the *n*-alkanes, and hence the fractions of the overall OH radical reaction proceeding at the various $-CH_2-$ groups. Table 2 gives the formation yields of the 2-, 3-, and 4-alkyl nitrates from their precursor secondary $R\dot{O}_2$ radicals (i.e., rate constant ratios $k_{3a}/(k_{3a} + k_{3b})$ derived from our present and previous[5,10] data and the calculated fractions of the overall OH radical reaction proceeding at the 2-, 3-, and 4-position $-CH_2-$ groups.[24] It needs to be recognized that while the calculated overall rate constants for the reaction of the OH radical with the C_2−C_8 *n*-alkanes at 298 K agree with the recommended values[1] to within 13%, the calculated partial rate constants and hence fractions of the overall reaction proceeding at the various $-CH_3$ and $-CH_2-$ groups may be less reliable.[10]

The secondary alkyl nitrate formation yields from the corresponding $R\dot{O}_2$ radicals given in Table 2 show that the nitrate yield increases with the carbon number, as observed previously.[5] Table 2 also shows that the nitrate yields from the various secondary $R\dot{O}_2$ radicals, and hence values of $k_{3a}/(k_{3a} + k_{3b})$, for a given *n*-alkane are similar, although the 2-alkyl nitrate yields are consistently lower than those of the 3-alkyl nitrates. The measured 3-nitrate/2-nitrate and 4-nitrate/2-nitrate formation yield ratios are all similar, with an average value of 1.35 ± 0.15 (two standard deviations), and this ratio can be compared with that of 1.23 obtained from the estimation method of Kwok and Atkinson[24] assuming that for a given *n*-alkane the secondary alkyl nitrate yield per $R\dot{O}_2$ precursor radical is identical. Given the likely uncertainties in the substituent group factors in the estimation method,[24,25] our data are consistent with the secondary alkyl nitrate yield per $R\dot{O}_2$ precursor radical being identical for a given *n*-alkane.

A plot of the formation yields of the sum of the secondary alkyl nitrates for a given alkane from the corresponding secondary alkyl peroxy radicals for propane through *n*-octane (data from Atkinson et al.[5,10] and this work) and cyclohexane (data from Aschmann et al.[11]) against carbon number is shown in Figure 2. The cyclohexyl nitrate yield of Aschmann et al.[11] of 0.165 ± 0.021 at 298 ± 2 K and 740 Torr pressure of air is in good agreement with the yields reported by Platz et al.[12] (0.16 ± 0.04 at 296 ± 2 K and 700 Torr total pressure) and Orlando et al.[13] (0.15 ± 0.04 at 296 K and 700 Torr total pressure), but is higher than the value of 0.090 ± 0.044 at atmospheric pressure and room temperature measured by Takagi et al.[4] The nitrate

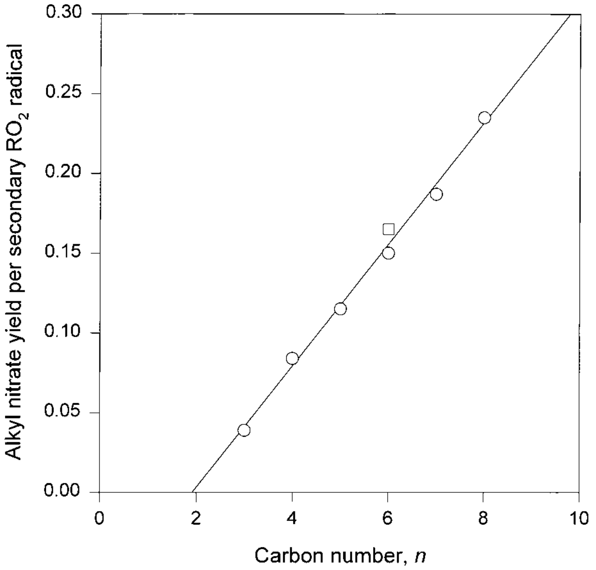

Figure 2. Plot of the yields of secondary alkyl nitrates from their precursor secondary alkyl peroxy radicals, $k_{3a}/(k_{3a} + k_{3b})$, for the C_3–C_8 *n*-alkanes (○) and cyclohexane (□) against carbon number of the alkane. The data for the propane and *n*-butane reactions are from Atkinson et al.;[5] for the *n*-pentane reaction are from Atkinson et al.;[10] and for the cyclohexane reaction are from Aschmann et al.[11]

yield per secondary R$\dot{O}_2$ radical from cyclohexane fits very well with the data from the *n*-alkanes, and the alkyl nitrate formation yield from secondary alkyl peroxy radicals is linear with the carbon number of the alkane. From the data shown in Figure 2 the ratio $k_{3a}/(k_{3a} + k_{3b})$ for secondary R$\dot{O}_2$ radicals at 298 K and atmospheric pressure of air is

$$k_{3a}/(k_{3a} + k_{3b}) = (0.0381 \pm 0.0031)n - (0.073 \pm 0.0178)$$

where *n* is the number of carbon atoms in the alkane and the indicated errors are two least-squares standard deviations. The rate constant ratio k_{3a}/k_{3b} for primary, secondary, and tertiary alkyl groups is needed for extrapolation to temperatures and pressures outside of the range for which experimental data are available and for $>C_8$ alkanes.[14] Our present data can be used with previous literature data for alkyl nitrate formation from propane,[5] *n*-butane,[5] *n*-pentane,[10] 2-methylbutane,[7,8] 2-methylpentane,[7] 3-methylpentane,[7,8] cyclohexane,[11–13] and *n*-heptane[9] to revise the formula proposed by Carter and Atkinson.[14]

$$\frac{k_{3a}}{k_{3b}} = \left[\frac{Y_o^{298}[M](T/298)^{-m_o}}{1 + \dfrac{Y_o^{298}[M](T/298)^{-m_o}}{Y_\infty^{298}(T/298)^{-m_\infty}}}\right]F^z \qquad (I)$$

where

$$z = \left(1 + \left[\log\left(\frac{Y_o^{298}[M](T/298)^{-m_o}}{Y_\infty^{298}(T/298)^{-m_\infty}}\right)\right]^2\right)^{-1}$$

and

$$Y_o^{298} = \alpha e^{\beta n}$$

in which $Y_o^{298}[M]$ and Y_∞^{298} are the limiting low-pressure and high-pressure rate constant ratios k_{3a}/k_{3b} at 298 K, respectively, [M] is the concentration of diluent air, *F*, m_o, m_∞, α, and β are parameters, and *n* is the number of carbon atoms in the alkane. We assume that the temperature dependence of the 2- and 3-pentyl nitrate formation yields from the *n*-pentane reaction measured by Atkinson et al.[6] is correct (with all of the measured yields being consistently slightly high due to calibration problems). The secondary alkyl nitrate yield data can then be reasonably well fit with the following values of the parameters in eq I: $\alpha = 2 \times 10^{-22}$ cm^3 molecule^{-1}, $\beta = 1.0$, $Y_\infty^{298} = 0.43$, $F = 0.41$, $m_o = 0$, and $m_\infty = 8.0$. The major difference between these revised parameters and those given in Carter and Atkinson[14] is in the value of Y_∞^{298}, with Carter and Atkinson[14] deriving $Y_\infty^{298} = 0.87$ (0.826 at 300 K), and our revised formula leads to alkyl nitrate yields which are increasingly lower than the previous[14] prediction for $n > 5$.

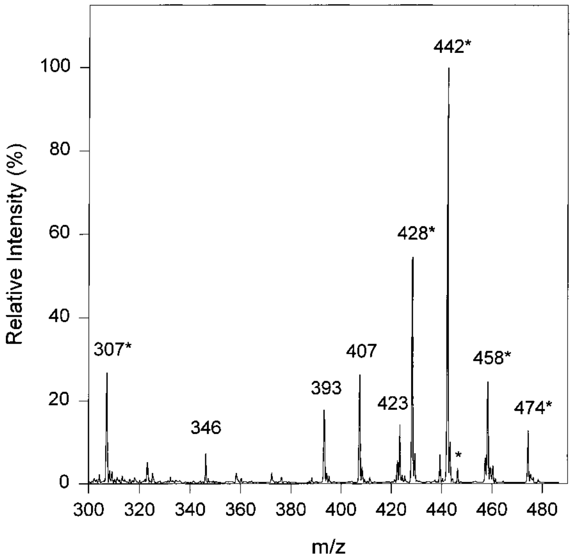

Figure 3. API-MS negative ion spectrum (300–500 u) of an irradiated $CH_3ONO/NO/n$-hexane/air mixture, with addition of pentafluorobenzyl alcohol (PFBOH) to the sampled air stream. The ion peaks marked with (*) are attributed to the following: 428 u, $[(PFBOH)_2{\cdot}O_2]^-$; 442 u, $[(PFBOH)_2{\cdot}NO_2]^-$; 446 u, $[(PFBOH)_2{\cdot}O_2{\cdot}H_2O]^-$; 458 u, $[(PFBOH)_2{\cdot}O_2{\cdot}NO]^-$; and 474 u, $[(PFBOH)_2{\cdot}O_2{\cdot}NO_2]^-$. The 307 u ion peak is always present when the PFBOH is added and may be due to a proton-transfer reaction.

API-MS Analyses. A series of $CH_3ONO/NO/n$-alkane/air irradiations were carried out with analysis using in situ atmospheric pressure ionization tandem mass spectrometry (API-MS). In these analyses, the API-MS was operated in the negative ion mode, and either PFBOH was added to the gas stream sampled from the chamber or NO_2 was introduced into the chamber after the reaction was completed.

PFBOH Addition. The formation of dimers in the API source has proved to be an effective means of product identification in a number of complex reaction systems.[11,26,27] PFBOH has a strong response in the negative ion mode and readily forms dimers as well as adduct ions with O_2^- and NO_2^-, and its addition to the sample stream was utilized to identify the hydroxycarbonyl and hydroxynitrate products from the OH radical-initiated reactions of *n*-pentane through *n*-octane and of *n*-pentane-d_{12} through *n*-octane-d_{18}. All of these reactions gave analogous results, as illustrated using the *n*-hexane reaction as an example. Figure 3 shows the API-MS spectrum, in the adduct ion region above 300 u, of an irradiated $CH_3ONO/NO/n$-hexane/air mixture. The majority of the ion peaks (those marked with (*) are present when PFBOH is added to the pre-reaction chamber sample, i.e., to the *n*-alkane/CH_3ONO/NO/air mixture prior to irradiation) can be attributed to dimers of PFBOH forming adducts with O_2, NO_2, NO, and H_2O. The NO and NO_2 adducts are present from the CH_3ONO/NO/air mixture used to generate OH radicals and the NO concentration decreases, and

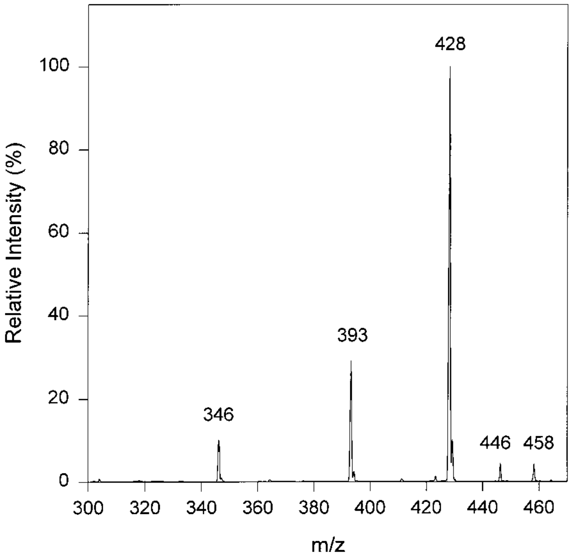

Figure 4. API-MS/MS CAD "precursor ion" negative ion spectrum of the 230 u $[PFBOH{\cdot}O_2]^-$ ion for the same experiment as in Figure 3. The ion peaks at 428, 446, and 458 u are attributed as noted in Figure 3. The 346 and 393 u ion peaks indicate two products of the *n*-hexane reaction.

the NO_2 concentration increases, as the reaction proceeds. As shown in Figure 4, an API-MS/MS "precursor ion" scan of 230 u (which corresponds to $[PFBOH{\cdot}O_2]^-$) resulted in two ion peaks at 346 and 393 u, in addition to those identified in Figure 3 as being from the PFBOH. API-MS/MS "product ion" spectra of these 346 and 393 u ion peaks are shown in Figure 5 parts A and B, respectively. In general, API-MS/MS "product ion" spectra of the adduct ions $[PFBOH{\cdot}O_2{\cdot}M]^-$ show a prominent fragment ion at 230 u $[PFBOH{\cdot}O_2]^-$, with the difference in mass of the adduct ion and the 230 u fragment ion being the molecular weight of the product M. Thus products of molecular weight 116 (an hydroxycarbonyl) and 163 (an hydroxynitrate) are indicated from the API-MS/MS spectra in Figure 5, partsA and B, respectively. These products are also evident from the less abundant fragment ions at 148 u and 195 u, corresponding to $[M{\cdot}O_2]^-$ formed from loss of PFBOH from the parent ion, that are also seen in Figure 5, parts A and B, respectively.

Table 3 shows the molecular weights of the reaction products observed from the *n*-alkanes and deuterated *n*-alkanes studied using this procedure. Noting that species containing −OD groups rapidly D/H exchange to form −OH groups under our experimental conditions,[10,11,16,28] the product species observed from the *n*-alkanes are $C_nH_{2n}(OH)(ONO_2)$ and $C_nH_{2n-1}(O)(OH)$ species and those from the *n*-alkane-d_{2n+2} reactions are $C_nD_{2n}(OH)(ONO_2)$ and $C_nD_{2n-1}(O)(OH)$ species. The $C_nH_{2n}(OH)(ONO_2)$ species (and their deuterated analogues) are attributed to the 1,4-hydroxynitrates formed as shown in Scheme 1. The $C_nH_{2n-1}(O)(OH)$ species (and their deuterated analogues) are attributed to the 1,4-hydroxycarbonyls formed as also shown in Scheme 1 and previously observed by us[10,11,16] using API-MS and API-MS/MS in the positive ion mode, with $[(H_3O){\cdot}(H_2O)_n]^+$ clusters as the ionizing agent, and by Eberhard et al.[15] using GC-MS analyses after derivatization by 2,4-dinitrophenylhydrazine.

While the formation of $[PFBOH{\cdot}O_2{\cdot}M]^-$ ions was useful for hydroxycarbonyl and hydroxyalkyl nitrate identification, this method did not appear to be suitable for quantification purposes. It was observed that the reactions of NO_2^- ions with PFBOH (to form $[PFBOH{\cdot}NO_2]^-$) competed with the corresponding reaction of O_2^- ions with PFBOH at NO_2 concentrations of $\geq 10^{12}$ molecule cm^{-3}. For example, in Figure 3 the ion peak at 407 u is attributed to the $[PFBOH{\cdot}NO_2]^-$ adduct with the hydroxynitrate. However, the corresponding adduct did not form with the hydroxycarbonyl and as the NO_2 increased during the reaction, the signal for the $[PFBOH{\cdot}O_2{\cdot}\text{hydroxycarbonyl}]^-$ adduct at 346 u disappeared. Therefore, because NO_2 is formed from the photooxidation of methyl nitrite (and also from reactions of HO_2 and organic peroxy radicals with NO), this limited the potential of using $[PFBOH{\cdot}O_2{\cdot}M]^-$ ions for quantification.

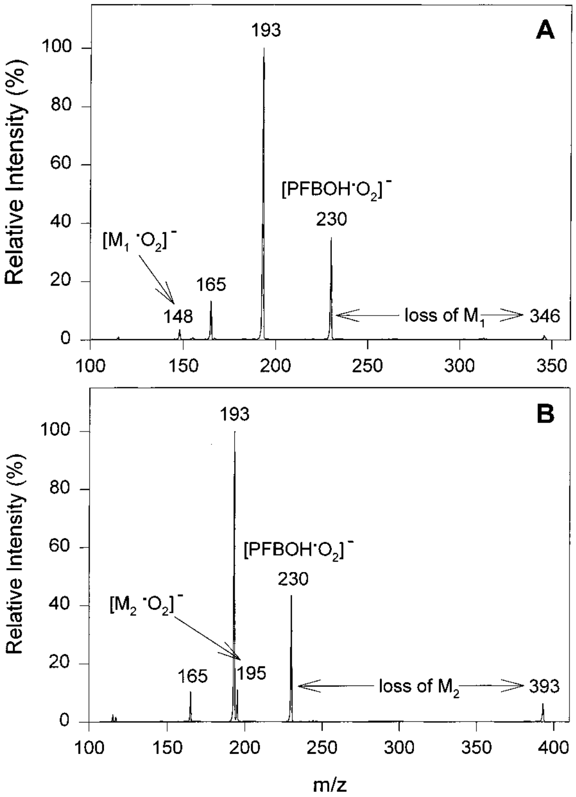

Figure 5. API-MS/MS CAD "product ion" negative ion spectra of the ion peaks at 346 u and 393 u observed in the API-MS/MS CAD "precursor ion" spectrum of the 230 u $[PFBOH{\cdot}O_2]^-$ ion shown in Figure 4. (A) The molecular weight 116 product (M_1) is seen from the loss of M_1 from the parent adduct ion $[PFBOH{\cdot}O_2{\cdot}M_1]^-$— $[M_1]$ = 230 u and by the presence of a fragment ion that is the O_2^- adduct at 148 u. (B) The molecular weight 163 product (M_2) is seen from the loss of M_2 from the parent adduct ion $[PFBOH{\cdot}O_2{\cdot}M_2]^-$—$[M_2]$ = 230 u and by the presence of a fragment ion that is the O_2^- adduct at 195 u. The 230, 193, and 165 u ion fragments are characteristic of PFBOH.

TABLE 3: Product Species Observed from the Reactions of the OH Radical with *n*-Alkanes in the Presence of NO, from the Presence of $[PFBOH{\cdot}O_2{\cdot}M]^-$ Ions

	molecular weight of product M	
alkane	*n*-alkane	*n*-alkane-d_{2n+2}
n-pentane	102	111
	149	159
n-hexane	116	127
	163	175
n-heptane	130	143
	177	191
n-octane	144	159
	191	207

NO_2 Addition. It was observed that in the absence of PFBOH, the hydroxycarbonyls and hydroxyalkyl nitrates formed adducts with O_2^- and with NO_2^- ions and that the majority of the adducts at the end of the alkane photooxidation were NO_2^- adducts. Figure 6 shows an API-MS spectrum of an irradiated

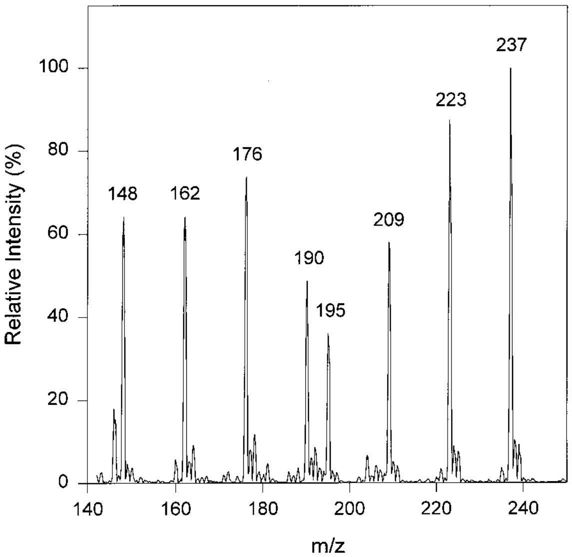

Figure 6. API-MS negative ion spectrum of an irradiated $CH_3ONO/NO/n$-pentane/n-hexane/n-heptane/n-octane/air mixture, with NO_2 added to the chamber after the irradiation and an NO_2 concentration of 3×10^{13} molecule cm^{-3}. The initial n-alkane concentrations were each $\sim 2.2 \times 10^{12}$ molecule cm^{-3} and the extents of reaction ranged from 5.6% for n-pentane to 13% for n-octane. The C_5- through C_8-hydroxycarbonyls are observed as their NO_2^- adducts at 148, 162, 176, and 190 u, respectively, and the C_5- through C_8-hydroxyalkyl nitrates are observed as their NO_2^- adducts at 195, 209, 223, and 237 u, respectively. The concentration of the C_5-hydroxyalkyl nitrate (expected to be almost totally 4-nitrooxypentan-1-ol) is estimated to be 3.3×10^9 molecule cm^{-3}.

$CH_3ONO/NO/n$-pentane/n-hexane/n-heptane/n-octane/air mixture, with the C_5- through C_8-hydroxycarbonyls being observed as their NO_2^- adducts at 148, 162, 176, and 190 u, respectively, and the C_5- through C_8-hydroxyalkyl nitrates being observed as their NO_2^- adducts at 195, 209, 223, and 237 u, respectively. API-MS spectra and API-MS/MS "precursor ion" spectra of the 32 u O_2^- ion and the 46 u NO_2^- ion showed that reactions of the NO_2^- ion to form the $[NO_2{\cdot}M]^-$ adducts dominated over the corresponding reactions of the O_2^- ion at NO_2 concentrations $\geq(2-3) \times 10^{13}$ molecule cm^{-3}, and that under these NO_2 concentration conditions the dominant ion peaks involving the hydroxcarbonyls and hydroxyalkyl nitrates were the $[NO_2{\cdot}M]^-$ ions.

Therefore addition of NO_2 after the reaction was employed to attempt to quantify the hydroxycarbonyl and hydroxyalkyl nitrates in these OH radical-initiated reactions, with an internal standard of similar chemical structure as the reaction products of interest also being introduced into the chamber. A series of experiments were carried out in which measured amounts of 5-hydroxy-2-pentanone, 4-hydroxy-4-methyl-2-pentanone, and 1-hydroxy-2-butanone were introduced into the chamber in the presence of $(1-3) \times 10^{13}$ molecule cm^{-3} of NO_2 (the concentrations of the hydroxycarbonyls in the chamber were in the range $(2.4-24) \times 10^{11}$ molecule cm^{-3}). The API-MS spectra obtained from two independent experiments showed that the intensities of the $[NO_2{\cdot}\text{hydroxycarbonyl}]^-$ adducts depended on the particular hydroxycarbonyl M, with the relative API-MS ion intensities of the $[NO_2{\cdot}\text{hydroxycarbonyl}]^-$ adducts for equal concentrations of the hydroxycarbonyls being the following: 1-hydroxy-2-butanone (a 1,2-hydroxycarbonyl), 1.0; 5-hydroxy-2-pentanone (a 1,4-hydroxycarbonyl), 0.5 ± 0.1; and 4-hydroxy-4-methyl-2-pentanone (a 1,3-hydroxycarbonyl), 1.9 ± 0.3. Given this range of responses, we used 5-hydroxy-2-pentanone (the dominant 1,4-hydroxycarbonyl formed from the n-pentane reaction and the only commercially available 1,4-hydroxycarbonyl) as the internal standard for quantification of the 1,4-hydroxycarbonyls formed from the n-alkanes. The hydroxyalkyl nitrate 2-nitrooxy-3-butanol $CH_3CH(ONO_2)CH(OH)CH_3$ was formed in situ in the chamber from the reaction of the OH radical with *cis*-2-butene [using an average of the literature formation yields measured by Muthuramu et al.[29] (0.037 ± 0.009) and O'Brien et al.[30] (0.034 ± 0.005)] as the internal standard for quantification of the 1,4-hydroxyalkyl nitrates formed from the n-alkanes.

TABLE 4: Formation Yields of Hydroxycarbonyls and Hydroxyalkyl Nitrates from the Reaction of the OH Radical with *n*-Alkanes in the Presence of NO, As Obtained from Negative Ion API-MS Using NO_2^- as the Reagent Ion

	n-pentane	*n*-hexane	*n*-heptane	*n*-octane
	Hydroxycarbonyls			
relative yield[a]	1.33 ± 0.67	1.97 ± 0.61	1.69 ± 0.29	1.00
relative to internal standard[b]	0.60	0.49	0.29	0.24
yield[c]	0.36	0.53	0.46	0.27
	Hydroxyalkyl nitrates			
relative yield[a]	0.48 ± 0.12	0.85 ± 0.20	0.87 ± 0.05	1.00
relative to internal standard[d]	0.024	0.046	0.048	0.056
yield[c]	0.026	0.046	0.047	0.054

[a] From five experiments with all four n-alkanes in each irradiated $CH_3ONO/NO/n$-alkane/air mixture. Indicated errors are one standard deviation. [b] Yield for each alkane from an irradiated $CH_3ONO/NO/n$-alkane/air mixture with that alkane only present and with a measured amount of added 5-hydroxy-2-pentanone as the internal standard. [c] Yield obtained from combining the relative yields with the relative yield based on the internal standard for each n-alkane. Overall uncertainties are estimated to be a factor of 2. [d] From two of the above five experiments with $CH_3CH(OH)CH(ONO_2)CH_3$ being formed in situ from the reaction of the OH radical with *cis*-2-butene (see text). The relative hydroxyalkyl nitrate yields in these two experiments were within 10% of the average from all five experiments.

After a series of preliminary experiments to investigate this approach for quantification of hydroxycarbonyls and hydroxyalkyl nitrates, we carried out one experiment for each n-alkane with 5-hydroxy-2-pentanone being added as the internal standard after the irradiation (for n-pentane, this corresponds to adding an additional known amount of 5-hydroxy-2-pentanone to that formed in the reaction). In addition to the formation of the C_n-hydroxycarbonyl from the C_n n-alkane, these experiments showed the formation (numbers in parentheses are the percents relative to the C_n-hydroxycarbonyl) of C_4- (25%), C_5- (15%), C_6- (11%), and C_7-hydroxycarbonyls (21%) from the n-octane reaction, C_4- (14%), C_5- (10%), and C_6-hydroxycarbonyls (12%) from the n-heptane reaction, and C_4- (10%) and C_5-hydroxycarbonyls (17%) from the n-hexane reaction. These observations indicate that decomposition reactions, such as that illustrated in Scheme 1 for the 2-hexoxy radical, must occur. Note that it is possible that the ion peaks attributed to NO_2^- adducts of C_{n-1} hydroxycarbonyls were in part O_2^- adducts of the C_n hydroxycarbonyls.

Five experiments with all four n-alkanes present were also carried out to determine the relative amounts of the various hydroxycarbonyls formed (with no addition of 5-hydroxy-2-pentanone). The initial concentrations of the n-alkanes were varied over the range $(0.206-2.49) \times 10^{13}$ molecule cm^{-3}, and the maximum extent of reaction was 12−14% of the initial n-alkane. Correcting for secondary reactions of the hydroxycarbonyls and for formation from the decomposition pathway, these experimental data lead to the hydroxycarbonyl formation yields given in Table 4.

The above CH_3ONO/NO/*n*-alkane/air irradiations with a single *n*-alkane present also showed the formation (numbers in parentheses are the percents relative to the C_n-hydroxyalkyl nitrate) of C_5- (3%), C_6- (3%), and C_7-hydroxyalkyl nitrates (7%) from the *n*-octane reaction, C_5- (1.5%) and C_6-hydroxyalkyl nitrates (6.5%) from the *n*-heptane reaction, and C_5-hydroxyalkyl nitrates (9%) from the *n*-hexane reaction. In two of the experiments with all four *n*-alkanes present, $CH_3CH(OH)CH(ONO_2)CH_3$ was formed in situ from the reaction of the OH radical with *cis*-2-butene and used as an internal standard for hydroxyalkyl nitrate quantification, and in the three additional experiments the relative yields of hydroxyalkyl nitrates from the four *n*-alkanes were measured. The hydroxyalkyl nitrate formation yields resulting from these experiments are also given in Table 4. It is of interest to note that the API-MS is quite sensitive to hydroxyalkyl nitrates (more so than to hydroxycarbonyls, as evident from Figure 6 and the formation yield data shown in Table 4), with (Figure 6) detection limits of <50 part-per-trillion (ppt) mixing ratio ($<1 \times 10^9$ molecule cm^{-3}); indeed, dilution of the chamber contents by a factor of 8 indicated that 10 ppt mixing ratios (2×10^8 molecule cm^{-3}) of these hydroxyalkyl nitrates could still be readily observed.

Conclusions

Our alkyl nitrate, hydroxyalkyl nitrate, and hydroxycarbonyl formation yields given in Table 4, combined with the literature carbonyl yields arising from alkoxy radical decomposition and reaction with O_2, account for ∼95%, ∼80%, ∼70%, and ∼55% of the products formed from the OH radical-initiated reactions of *n*-pentane, *n*-hexane, *n*-heptane, and *n*-octane (in the presence of NO), respectively, with uncertainties of approximately a factor of 1.4 in each case. We can therefore now account for most of the reaction products formed from these *n*-alkanes, and hydroxycarbonyl formation accounts for a significant fraction of these products (in fact, for most of the products from *n*-hexane, *n*-heptane, and *n*-octane). Hydroxyalkyl nitrate formation accounts for a few percent of the overall reaction products, and is consistently ∼25% of the corresponding alkyl nitrate yields. Our hydroxyalkyl nitrate yield from the *n*-hexane reaction of 0.046 (with an uncertainty of a factor of 2) is reasonably consistent with the approximate upper limit estimate of Eberhard et al.[15] for the formation of 5-nitrooxyhexan-2-ol of 0.03−0.04.

Thus significant fractions of the atmospheric reaction products of $\geq C_5$ *n*-alkanes (and other alkanes whose intermediate alkoxy radicals can isomerize) are comprised of hydroxycarbonyls and hydroxyalkyl nitrates, compound classes which are presently difficult to analyze under atmospheric conditions.

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