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Atmospheric Chemistry of Three C_{10} Alkanes

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Kinetics and products of the gas-phase reactions of OH radicals with the C_{10}-alkanes *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane have been investigated at 296 ± 2 K and atmospheric pressure of air. Gas chromatography with flame ionization detection (GC−FID) and combined gas chromatography−mass spectrometry (GC-MS) were used to identify and quantify alkyl nitrate and carbonyl products, and in situ atmospheric pressure ionization tandem mass spectrometry was employed to identify and quantify, relative to internal standards, hydroxycarbonyl and hydroxynitrate products. Using a relative rate method, rate constants for reactions of the OH radical with *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane were measured and (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) were 12.5 ± 0.4, 7.43 ± 0.48 and 15.8 ± 0.6, respectively, where the errors do not include uncertainties in the rate constant for the *n*-octane reference compound. The products identified and quantified were: 2-, 3-, 4-, and 5-decyl nitrate, hydroxycarbonyls and hydroxynitrates from the *n*-decane reaction; acetaldehyde, propanal, 3-pentanone, 3-pentyl nitrate, C_{10} alkyl nitrates, hydroxycarbonyls, and hydroxynitrates from the 3,4-diethylhexane reaction; and butanal, cyclohexanone, C_{10} alkyl nitrates, hydroxycarbonyls and hydroxynitrates from the *n*-butylcyclohexane reaction. The observed gas-phase products are generally in accord with expectations, and account for a significant fraction of the total products.

Introduction

Alkanes are released into the atmosphere from gasoline- and diesel-fueled vehicles and from volatilization of alkane solvents. In the troposphere, alkanes present in the gas phase react mainly with the OH radical[1] to form alkyl radicals, which then react rapidly with O_2 to form alkyl peroxy ($R\dot{O}_2$) radicals[1]

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

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

In the presence of NO (for example, in polluted urban areas), $R\dot{O}_2$ radicals react with NO to form an alkyl nitrate or an alkoxy ($R\dot{O}$) radical plus NO_2[1]

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

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

In the atmosphere, alkoxy radicals formed in reaction 3b can react with O_2, decompose by C−C bond scission, or isomerize through a six-membered ring transition state.[1−3] The isomerization reaction becomes important for $\geq C_4$ alkanes and may lead to formation of 1,4-hydroxycarbonyls.[1−3]

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.[4−15] For the *n*-alkanes, the alkyl nitrate yields increase with increasing carbon number in the *n*-alkane,[6,15] with molar yields ranging from ≤0.014 for ethane to 0.23 for *n*-octane at room temperature and atmospheric pressure of air.[15] The alkyl nitrate yields also increase with increasing pressure and with decreasing temperature.[7,9,10,16] The formation of hydroxyalkyl nitrates from the OH radical-initiated reactions of alkanes, arising after alkoxy radical isomerization, has been reported from the *n*-hexane[17] and *n*-pentane through *n*-octane[15] reactions.

In this work, we have investigated the atmospheric chemistry of three C_{10} alkanes, *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane, chosen as representative linear, branched and cyclic alkanes present in solvents. Rate constants for the OH radical reactions were measured using a relative rate method, and products of the OH radical-initiated reactions were 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 (API−MS/MS).

Experimental Methods

Experiments were carried out at 296 ± 2 K and 740 Torr total pressure of air in a ~8000 L Teflon chamber with analysis by GC−FID and 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 (OH) radicals were generated by the photolysis of methyl nitrite in air at wavelengths >300 nm,[18] and NO was added to the reactant mixtures to suppress the formation of O_3 and hence of NO_3 radicals.[18]

Measurement of OH Radical Reaction Rate Constants. Rate constants for the OH radical reactions were determined using a relative rate method in which the relative disappearance rates of the alkanes and a reference compound (*n*-octane in this

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study), whose OH radical reaction rate constant is reliably known,[3] were measured in the presence of OH radicals.[18] Providing that the alkanes and the *n*-octane reference compound reacted only with OH radicals, then[18]

$$\ln\left(\frac{[\text{alkane}]_{\text{to}}}{[\text{alkane}]_{\text{t}}}\right) = \frac{k_{1a}}{k_{1b}} \ln\left(\frac{[n\text{-octane}]_{\text{to}}}{[n\text{-octane}]_{\text{t}}}\right) \tag{I}$$

where $[\text{alkane}]_{\text{to}}$ and $[n\text{-octane}]_{\text{to}}$ are the concentrations of the alkane and *n*-octane, respectively, at time t_o, $[\text{alkane}]_{\text{t}}$ and $[n\text{-octane}]_{\text{t}}$ are the corresponding concentrations at time *t*, and k_{1a} and k_{1b} are the rate constants for reactions 1a and 1b, respectively

$$\text{OH} + \text{alkane} \rightarrow \text{products} \tag{1a}$$

$$\text{OH} + n\text{-octane} \rightarrow \text{products} \tag{1b}$$

Hence, plots of $\ln([\text{alkane}]_{\text{to}}/[\text{alkane}]_{\text{t}})$ against $\ln([n\text{-octane}]_{\text{to}}/[n\text{-octane}]_{\text{t}})$ should be straight lines with slope k_{1a}/k_{1b} and zero intercept.

The initial reactant concentrations (in molecules cm^{-3} units) were CH_3ONO, 2.2×10^{14}; NO, $(2.2-2.3) \times 10^{14}$; and alkane and *n*-octane, $\sim 2.4 \times 10^{13}$ each. Irradiations were carried out at 20% of the maximum light intensity for 10−50 min, resulting in up to 40%, 37%, 52%, and 61% consumption of the *n*-octane, 3,4-diethylhexane, *n*-decane, and *n*-butylcyclohexane, respectively. The concentrations of the alkanes 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 ∼250 °C onto a 30 m DB-1701 megabore column held at 40 °C and then temperature-programmed to 200 °C at 8 °C min^{-1}. NO and initial NO_2 concentrations were measured using a Thermo Environmental Instruments, Inc., model 42 chemiluminescent $NO-NO_x$ analyzer.

Products of the OH Radical-Initiated Reactions. Two sets of experiments were carried out, one set using GC−FID and GC-MS for analysis, and the second set using in situ API-MS and API-MS/MS.

Analyses by GC−FID and GC-MS. For the OH radical reactions carried out in the ∼8000 L Teflon chamber (at ∼5% relative humidity), the initial reactant concentrations (in molecules cm^{-3} units) were: CH_3ONO, $(2.2-2.3) \times 10^{14}$; NO, $(2.0-2.3) \times 10^{14}$; and alkane, $(2.25-2.51) \times 10^{13}$. Irradiations were carried out at 20% of the maximum light intensity for 5−50 min, resulting in up to 59%, 44%, and 65% reaction of the initially present *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane, respectively. The concentrations of the alkanes and products were measured during the experiments by GC−FID as described above for the rate constant measurements, with an initial GC column temperature of 40 °C for the measurement of alkyl nitrates and of −40 °C for the measurement of more volatile carbonyl products. GC−FID response factors for the alkanes and carbonyl products were determined by introducing measured amounts of the chemicals into the 8000 L chamber and conducting several replicate GC−FID analyses.[19] A number of C_{10} alkyl nitrates are expected to be formed from the OH radical-initiated reactions of *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane, and these C_{10} alkyl nitrates are expected to have molar GC−FID responses very similar to one another.[20] Because of a lack of commercially available standards, these C_{10} alkyl nitrates were quantified by GC−FID using their Equivalent Carbon Numbers [ECNs], calculated relative to that for the parent alkane.[20]

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. NO and initial NO_2 concentrations were measured using a Thermo Environmental Instruments, Inc., model 42 $NO-NO_2-NO_x$ chemiluminescence analyzer.

Analyses 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.[12,15,21] 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.[12] Both positive and negative ion modes were used in these experiments. In the positive ion mode, protonated water hydrates, $H_3O^+(H_2O)_n$, generated by the corona discharge in the chamber diluent gas were responsible for the protonation of analytes. Ions are drawn by an electric potential from the ion source through the sampling orifice into the mass-analyzing first quadrupole or third quadrupole. For these experiments, the API-MS instrument was operated under conditions that favored the formation of dimer ions in the ion source region.[12,21] Neutral molecules and particles are prevented from entering the orifice by a flow of high-purity nitrogen ("curtain" gas), and as a result of the declustering action of the curtain gas on the hydrated ions, the ions that are mass-analyzed are mainly protonated molecules ($[M+H]^+$) and their protonated homo- and heterodimers.[12,21]

In the negative ion mode, negative ions were 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 formed in the pure air. Other reagent ions, for example, NO_2^- and NO_3^-, are formed through reactions between the primary reagent ions and neutral molecules such as NO_2 (note that the NO_2 concentration increases during the course of the chamber reactions). Under the experimental conditions used, analytes were detected as adduct ions formed from reaction of the neutral analyte (M) and the reagent ions, mainly O_2^- and/or NO_2^-.[15] 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 at NO_2 concentrations $\geq(2-3) \times 10^{13}$ molecules cm^{-3}, $[NO_2 \bullet M]^-$ adducts dominated over $[O_2 \bullet M]^-$ adducts.[15] Therefore, addition of NO_2 after the reaction was employed to quantify the hydroxycarbonyls and hydroxyalkyl nitrates formed in these OH radical-initiated reactions, with an internal standard of similar chemical structure as the reaction products of interest also being introduced into, or formed in, the chamber.[15] We used 5-hydroxy-2-pentanone (the dominant 1,4-hydroxycarbonyl formed from the *n*-pentane reaction[15,21] and the only commercially available 1,4-hydroxycarbonyl) as the internal standard for quantification of the 1,4-hydroxycarbonyl(s) formed from the C_{10} alkanes. The hydroxyalkyl nitrate $CH_3CH(OH)CH(ONO_2)CH_3$ was formed in situ in the chamber from the reaction of the OH radical with *cis*-2-butene to serve as an internal standard for quantification of the 1,4-hydroxyalkyl nitrates formed. An average of the literature formation yields measured by Muthuramu et al.[22] (0.037 ± 0.009) and O'Brien et al.[23] (0.034 ± 0.005) was used to calculate the concentration of $CH_3CH(OH)CH(ONO_2)CH_3$ in the chamber.

The initial concentrations of CH_3ONO, NO and alkane were equal and generally at $\sim 4.8 \times 10^{12}$ molecules cm^{-3} each (in

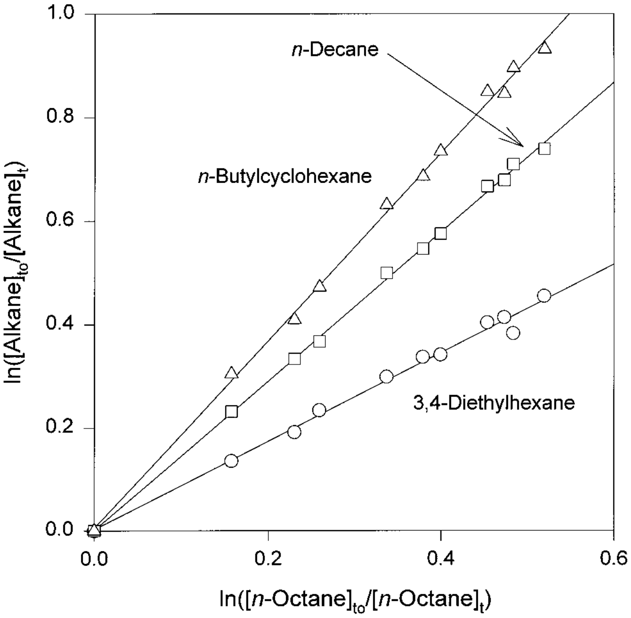

Figure 1. Plots of eq I for the gas-phase reactions of OH radicals with *n*-decane, 3,4-diethylhexane, and *n*-butylcyclohexane, with *n*-octane as the reference compound.

two *n*-decane experiments the initial concentrations were ~1.2 × 10^{13} and ~2.4 × 10^{13} molecules cm^{-3} each). Irradiations were carried out at 20% of the maximum light intensity for 2−5 min, resulting in 7−19% reaction (7−12% in all but one experiment involving *n*-butylcyclohexane) of the initially present alkane.

Chemicals. The chemicals used, and their stated purities, were: acetaldehyde (99.5+%), butanal (99%), cyclohexanone (99.8%), *n*-decane (99+%), 3-pentanone (99+%) and propanal (99+%), Aldrich Chemical Co.; *n*-butylcyclohexane (99%) and 3,4-diethylhexane (99%), ChemSampCo; 2-pentyl nitrate (containing 3-pentyl nitrate), Fluorochem; and NO (≥99.0%) and *cis*-2-butene (≥95%), Matheson Gas Products. Methyl nitrite was prepared and stored as described previously.[18]

Results and Discussion

OH Radical Reaction Rate Constants. The data obtained from irradiations of CH_3ONO/NO/alkane/*n*-octane/air mixtures are plotted in accordance with eq I in Figure 1, and least-squares analyses of these data result in the rate constant ratios k_{1a}/k_{1b} given in Table 1. These rate constant ratios k_{1a}/k_{1b} can be placed on an absolute basis using a rate constant for reaction of OH radicals with *n*-octane at 296 K of 8.67×10^{-12} cm^3 $molecule^{-1}$ s^{-1},[3] and the resulting rate constants k_{1a} are also listed in Table 1. Our rate constants for 3,4-diethylhexane and *n*-butylcyclohexane are the first reported, while that for *n*-decane is in good agreement (within 13%) with those previously measured by Atkinson et al.,[24] Nolting et al.[25] and Behnke et al.[26] also using relative rate methods. As shown in Table 1, rate constants calculated using a structure−reactivity estimation method[27,28] agree well with the measured rate constants for *n*-decane and *n*-butylcyclohexane. However, the measured rate constant for 3,4-diethylhexane is a factor of 1.7 lower than the predicted value, and this may be due to steric hindrance as also observed, though to a lesser extent, for 2,2,4-trimethylpentane.[3] The product data for 3,4-diethylhexane are also suggestive of a lower reactivity of the tertiary C−H bonds compared to the predictions of the estimation method (see below).

Products of the OH Radical-Initiated Reactions. Irradiations of CH_3ONO/ NO/alkane/air mixtures were carried out, with analyses of carbonyl and alkyl nitrate products by GC−FID and GC-MS. The products observed are listed in Tables 2 (*n*-decane), 3 (3,4-diethylhexane) and 4 (*n*-butylcyclohexane). The GC−FID and GC-MS analyses showed the formation of four C_{10} alkyl nitrates from *n*-decane. The unique MS fragmentation patterns of the *n*-alkyl nitrates[15] allowed the isomers formed from *n*-decane to be distinguished, and 2-, 3-, 4-, and 5-decyl nitrate were identified. Three C_{10} alkyl nitrate peaks were observed from the 3,4-diethylhexane reaction and tentatively identified from their mass spectra as the two closely eluting stereoisomers of the secondary nitrate $CH_3CH(ONO_2)CH(CH_2CH_3)CH(CH_2CH_3)_2$ and the tertiary nitrate $(CH_3CH_2)_2C(ONO_2)CH(CH_2CH_3)_2$. Seven closely eluting C_{10} alkyl nitrates were identified by GC-MS from the *n*-butylcyclohexane reaction, but no isomer-specific identification was possible. These various C_{10} alkyl nitrates were quantified by GC−FID using response factors calculated from their ECNs[20] (see Experimental Methods).

The products also react with OH radicals, and these secondary reactions were taken into account as described previously.[6] The multiplicative correction factors, *F*, to take into account secondary reactions with the OH radical increase with the rate constant ratio *k*(OH + product)/*k*(OH + alkane) and with the extent of reaction.[6] The following literature rate constants (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) were used: alkanes, this work (Table 1); acetaldehyde, 15.9;[29] propanal, 19.6;[29] butanal, 23.5;[29] 3-pentanone, 2.00;[29] and cyclohexanone, 6.39.[30] Rate constants were calculated for the various C_{10} alkyl nitrates using the group rate constants and group substituent factors given by Atkinson,[28] decreased by 3.6% to account for the recent reference organic recommendations of Atkinson,[3] and were (in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}): 2-decyl nitrate, 8.75; 3-decyl nitrate, 7.84; 4- and 5-decyl nitrate, 7.64 each; $CH_3CH(ONO_2)CH(CH_2CH_3)CH(CH_2CH_3)_2$, 8.44; $(CH_3CH_2)_2C(ONO_2)CH(CH_2CH_3)_2$, 4.16; and C_{10}-alkyl nitrates formed from *n*-butylcyclohexane, 10.4 [an average of the calculated rate constants for the six secondary alkyl nitrates and the one tertiary alkyl nitrate, isomer-specific identifications not being available]. The maximum values of the multiplicative factor *F* were: acetaldehyde, 1.84 for formation from 3,4-diethylhexane; propanal, 2.09 for formation from 3,4-diethylhexane and 1.61 for formation from *n*-butylcyclohexane; butanal, 1.76 for formation from *n*-butylcyclohexane; 3-pentanone, 1.09 for formation from 3,4-diethylhexane; cy-

TABLE 1: Rate Constant Ratios k_{1a}/k_{1b} and Rate Constants k_{1a} for the Gas-phase Reactions of OH Radicals with *n*-Decane, 3,4-Diethylhexane, and *n*-Butylcyclohexane at 296 ± 2 K

		$10^{12} \times k_{1a}$ (cm^3 $molecule^{-1}$ s^{-1})		
alkane	k_{1a}/k_{1b}[a]	this work[a,b]	literature	reference
n-decane	1.44 ± 0.04	12.5 ± 0.4	11.1 ± 0.5[c]	Atkinson et al.[24]
			11.1 ± 0.4[d]	Nolting et al.[25]
			12.4 ± 0.2[e]	Behnke et al.[26]
			11.1	estimated[27,28]
3,4-diethylhexane	0.857 ± 0.055	7.43 ± 0.48	12.5	estimated[27,28]
n-butylcyclohexane	1.82 ± 0.06	15.8 ± 0.6	14.8	estimated[27,28]

[a] Indicated errors are two least-squares standard deviations. [b] Placed on an absolute basis using a rate constant of k_{1b}(OH + *n*-octane) = 8.67×10^{-12} cm^3 $molecule^{-1}$ s^{-1} at 296 K.[3] Indicated errors do not include the uncertainties in the rate constant k_{1b}. [c] At 299 ± 2 K, relative to k(OH + *n*-hexane) = 5.54×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[3] [d] At 312 K, relative to k(OH + *n*-heptane) = 7.16×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[3] [e] At 300 K, relative to k(OH + *n*-octane) = 8.76×10^{-12} cm^3 $molecule^{-1}$ s^{-1}.[3]

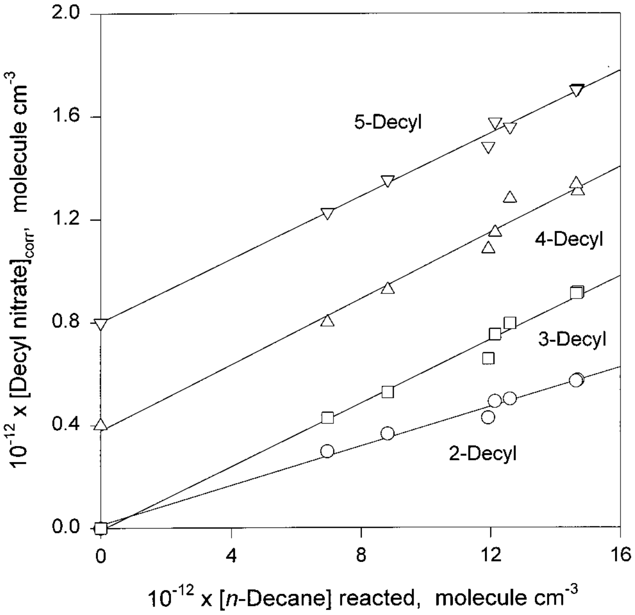

Figure 2. Plots of the amounts of 2-, 3-, 4-, and 5-decyl nitrate formed, corrected for secondary reactions with OH radicals (see text), against the amounts of *n*-decane reacted with the OH radical. The data for 4- and 5-decyl nitrate have been displaced vertically by 4.0 × 10^{11} molecules cm^{-3} and 8.0 × 10^{11} molecules cm^{-3}, respectively, for clarity.

TABLE 2: Products and Their Fractional Molar Yields from the Gas-Phase Reaction of OH Radicals with *n*-Decane in the Presence of NO

product	GC−FID analyses[a]	API-MS analyses
2-decyl nitrate	0.038 ± 0.007	
3-decyl nitrate	0.062 ± 0.011	
4-decyl nitrate	0.064 ± 0.013	
5-decyl nitrate	0.061 ± 0.010	
total decyl nitrates	0.226 ± 0.038	observed (MW 203)[b]
hydroxycarbonyls		observed (MW 172)[b] observed, yield 0.22[c]
hydroxynitrates		observed (MW 219)[b,d] yield 0.024[d]

[a] Indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC−FID response factors for the decyl nitrates, relative to that for *n*-decane, of ±15%. [b] Positive ion mode. [c] Negative ion mode as NO_2^- adducts. Ion peaks attributed to C_6-, C_7-, C_8-, C_9-, and C_{10}-hydroxycarbonyls were observed with average ratios 0.17: 0.16: 0.15: 0.17: 1.00; yield is the sum of these hydroxycarbonyls. [d] Negative ion mode as NO_2^- adduct of C_{10}-hydroxynitrate.

clohexanone, 1.18 for formation from *n*-butylcyclohexane; C_{10} alkyl nitrates, 1.41, 1.40, and 1.46 for formation from *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane, respectively.

API-MS analysis of irradiated CH_3ONO/NO/alkane/air mixtures were carried out in both positive ion and negative ion modes. API-MS/MS "product ion" and "precursor ion" spectra were obtained for ions observed in the API-MS spectra, and the results are discussed below for each of the alkanes studied, along with the chemical mechanisms consistent with the observed product distributions.

***n*-Decane.** Figure 2 shows plots of the amounts of decyl nitrates formed, corrected for secondary reactions, against the amounts of *n*-decane reacted, and the decyl nitrate formation yields obtained from least-squares analyses of these data are given in Table 2. API-MS analysis of irradiated $CH_3ONO/NO/$*n*-decane/air mixtures in the positive ion mode showed the presence of ion peaks at 155, 171, 173, 220, and 238 u (Figure 3A). API-MS/MS "product ion" and "precursor ion" spectra of these and other less intense ion peaks observed in the API-MS spectrum (note that the sensitivity for alkyl nitrates is very low) indicated the presence of products of molecular weight 172, 203, and 219, with the 155, 171, and 173 ion peaks being the $[M+H-H_2O]^+$, $[M+H-H_2]^+$ and $[M+H]^+$ ions of the molecular weight 172 product, and the 220 and 238 u ion peaks being the $[M + H]^+$ and $[M+H_3O]^+$ ions of the molecular weight 219 product. API-MS/MS "product ion" spectra of the 204 and 220 u ion peaks showed the presence of intense fragment ions at 46 u (attributed to NO_2^+), and hence these molecular weight 203 and 219 products are taken to be organic nitrates. Our observations of $[M+H-H_2O]^+$, $[M+H-H_2]^+$ and $[M+H]^+$ ions of a product of 30 mass units greater than that of the parent *n*-alkane is analogous to our observations for the *n*-butane through *n*-octane reactions.[21] This product of molecular weight 172 is identified as a hydroxycarbonyl (presumably a 1,4-hydroxycarbonyl) of formula $C_{10}H_{20}O_2$, whereas the molecular weight 203 and 219 products are identified as decyl nitrate(s) and hydroxydecyl nitrate(s), respectively. Analogous API-MS analyses of an irradiated $CH_3ONO/NO/$*n*-decane-d_{22}/air mixture showed the presence of ion peaks at 173, 174, 189, and 192 u, these being attributed to $[M+H-HDO]^+$, $[M+H-H_2O]^+$, $[M+H-HD]^+$, and $[M+H]^+$ of a molecular weight 191 product $[C_{10}D_{19}O(OH)]$, similar to our previous observations for the *n*-pentane-d_{12} through *n*-octane-d_{18} reactions.[21]

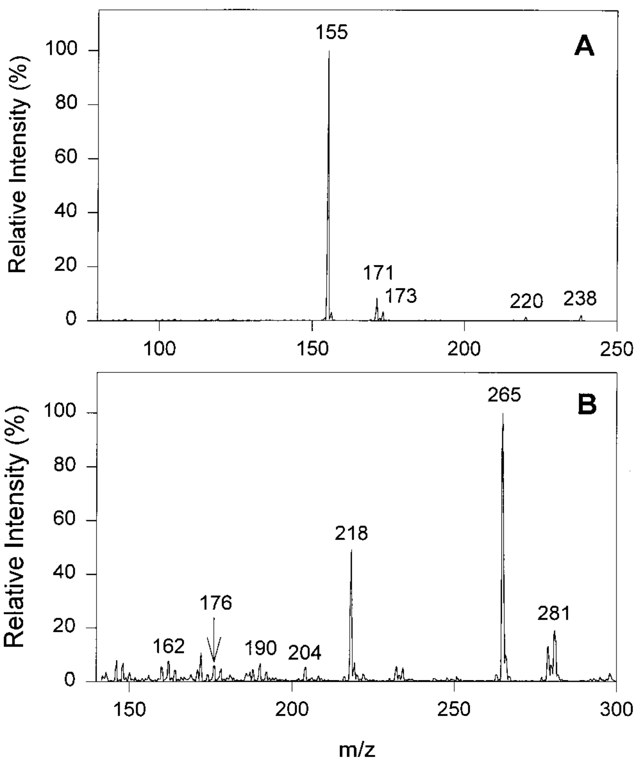

Figure 3. API-MS spectra of irradiated $CH_3ONO/NO/$*n*-decane/air mixtures. (A) Positive ion mode with protonation by $H_3O^+(H_2O)_n$ ions. (B) Negative ion mode using NO_2^- adduct ions. See text for assignments of the observed ion peaks.

In the negative ion mode, NO_2 was added after the reaction to quantify the hydroxycarbonyl and hydroxynitrate products as $[NO_2{\bullet}M]^-$ adducts,[15] as described above. Figure 3B shows an API-MS spectrum of an irradiated $CH_3ONO/NO/$*n*-decane/air mixture after addition of NO_2, showing the presence of ion peaks at 218 u (NO_2^- adduct of a molecular weight 172 species), 265 u (NO_2^- adduct of a molecular weight 219 species) and 281 u (potentially an NO_3^- adduct of the molecular weight 219 species). In addition to the formation of the C_{10}-hydroxycarbonyl, these experiments showed the presence of weaker ion signals at 162, 176, 190, and 204 u suggesting the formation (numbers in parentheses are the percents relative to the C_{10}-hydroxycarbonyl) of C_6- (15−20%), C_7- (13−17%), C_8- (9−15%) and C_9-hydroxycarbonyls (10−15%). These observations indicate that decomposition reactions of the alkoxy and/or hydroxyalkoxy radicals occur, although it is possible that the ion peak attributed to the NO_2^- adduct of the C_9 hydroxycarbonyls was in part the O_2^- adduct of the C_{10} hydroxycarbonyl. From five experiments with added 5-hydroxy-2-pentanone, and making an approximate correction for secondary reactions of the hydroxycarbonyls (9−16%), these data lead to the hydroxycarbonyl formation yield given in Table 2. In two of these experiments, $CH_3CH(OH)CH(ONO_2)CH_3$ was formed in situ from the reaction of the OH radical with *cis*-2-butene[22,23] and used as an internal standard for hydroxyalkyl nitrate quantification, as described above. The hydroxydecyl nitrate formation yield resulting from these experiments is also given in Table 2. As noted previously,[15] the API-MS is quite sensitive to hydroxyalkyl nitrates (more so than to hydroxycarbonyls, as evident from Figure 3B and the formation yields given in Table 2).

***n*-Decane Reaction Mechanism.** It is calculated that the fractions of the overall OH radical reaction proceeding by H atom abstraction from the C−H bonds at the 1-, 2-, 3-, 4- and 5-positions are 3.1%, 20.7%, 25.4%, 25.4%, and 25.4%, respectively.[27,28] Hence, the 2-, 3-, 4- and 5-decyl nitrate yields from their precursor secondary $C_{10}H_{21}\dot{O}_2$ radicals are 0.184 ± 0.034, 0.244 ± 0.044, 0.252 ± 0.052 and 0.240 ± 0.040, respectively. Within the experimental errors of the isomeric decyl nitrate measurements and the likely uncertainties in estimating the fractions of the overall OH radical reaction occurring at the various CH_2 groups, the average secondary decyl nitrate yield from secondary $C_{10}H_{21}\dot{O}_2$ radicals is 0.233 ± 0.040. This decyl nitrate yield per secondary $C_{10}H_{21}\dot{O}_2$ radical is ∼15% lower than the predicted value of 0.27.[15] Because of the rapid isomerization of all of the initially formed alkoxy radicals in the *n*-decane reaction[2,3] [see also below], formation of decyl nitrates from reaction 4

$$\mathrm{R\dot{O} + NO_2 \rightarrow RONO_2} \tag{4}$$

was of no importance for the experimental conditions employed here.

The product formation yields listed in Table 2 account for 47% of the reaction products from *n*-decane. However, it must be noted that the hydroxycarbonyl and hydroxynitrate yields given in Table 2 from the API-MS analyses are uncertain to a factor of ∼2−3 (as evident from five experiments in which the hydroxycarbonyl yields derived were 13%, 29%, 17%, 23%, and 34%), and that it is possible that these C_{10}-hydroxycarbonyls and hydroxynitrates were lost to some extent to the chamber walls and/or to particles formed in the chamber from the reactions. Our analyses showed evidence only for the formation of decyl nitrates, hydroxycarbonyls and hydroxynitrates, and hence it is likely that these are the only first-generation products formed from *n*-decane.

As shown by reactions 1−3, in the presence of NO the OH radical-initiated reaction leads to the formation of the various isomeric decyl nitrates and the corresponding decoxy radicals. The C_{10}-alkoxy radicals can react with O_2 [reaction 5], decompose by C−C bond scission [reaction 6], or isomerize through a six-membered transition state to form 1,4-hydroxydecyl radicals [reaction 7][2,3]

$$\mathrm{RCH(\dot{O})CH_2CH_2CH_2\acute{R} + O_2 \rightarrow RC(O)CH_2CH_2CH_2\acute{R} + HO_2} \tag{5}$$

$$\mathrm{RCH(\dot{O})CH_2CH_2CH_2\acute{R} \rightarrow RCHO + \acute{R}CH_2CH_2\dot{C}H_2} \tag{6}$$

$$\mathrm{RCH(\dot{O})CH_2CH_2CH_2\acute{R} \rightarrow RCH(OH)CH_2CH_2\dot{C}H\acute{R}} \tag{7}$$

The empirical estimation method of Aschmann and Atkinson[31] predicts that at 298 K and atmospheric pressure of air the isomerization rate for all of the decoxy radicals are $\sim 2.6 \times 10^6\ s^{-1}$, a factor of ∼40 higher than the estimated rates of the O_2 reactions ($\sim 5 \times 10^4\ s^{-1}$) and decompositions ($\sim 1 \times 10^4\ s^{-1}$). The 1,4-hydroxydecyl radicals formed from the isomerization reactions then add O_2 to form 1,4-hydroxydecyl peroxy radicals, which react with NO to form 1,4-hydroxydecyl nitrates [$RCH(OH)CH_2CH_2CH(ONO_2)\acute{R}$] or 1,4-hydroxydecoxy radicals [$RCH(OH)CH_2CH_2CH(\dot{O})\acute{R}$] plus NO_2 [by reactions analogous to reactions 2 and 3]. The 1,4-hydroxydecoxy radicals react with O_2, decompose by C−C bond scission, or isomerize, with the isomerization reaction 8

$$\mathrm{RCH(OH)CH_2CH_2CH(\dot{O})\acute{R} \rightarrow R\dot{C}(OH)CH_2CH_2CH(OH)\acute{R}} \tag{8}$$

being estimated[2,3,31] to be even more rapid than the initial isomerization, with a rate of $\sim 2 \times 10^7\ s^{-1}$ (and hence dominating over the decomposition and O_2 reactions by a factor of $>10^2$). The resulting α-hydroxy radical reacts with O_2 to form the 1,4-hydroxycarbonyl[1,29]

$$\mathrm{R\dot{C}(OH)CH_2CH_2CH(OH)\acute{R} + O_2 \rightarrow RC(O)CH_2CH_2CH(OH)\acute{R} + HO_2} \tag{9}$$

The products observed are in accord with these expectations, and we suggest that the first-generation products from *n*-decane are the decyl nitrates (largely the 2-, 3-, 4-, and 5-decyl nitrates), 1,4-hydroxydecyl nitrates and 1,4-hydroxydecanones (with some contribution of smaller hydroxycarbonyls from alkoxy radical decomposition reactions), and thereby analogous to our conclusions for the corresponding *n*-hexane through *n*-octane reactions.[15,21]

3,4-Diethylhexane. GC−FID and GC−MS analyses of irradiated $CH_3ONO/NO/3,4$-diethylhexane/air mixtures showed the formation of acetaldehyde, propanal, 3-pentanone, and (tentatively) the C_{10}-alkyl nitrates $CH_3CH(ONO_2)CH(CH_2CH_3)CH(CH_2CH_3)_2$ (observed as the two stereoisomers) and $(CH_3CH_2)_2C(ONO_2)CH(CH_2CH_3)_2$. In addition, a small GC peak was observed with a retention time matching that of 3-pentyl nitrate. Figure 4 shows plots of the amounts of selected products formed, corrected for secondary reactions, against the amounts of 3,4-diethylhexane reacted, and the product formation yields obtained from least-squares analyses of the data are given in Table 3. The plot of the amount of acetaldehyde formed against the amount of 3,4-diethylhexane reacted (Figure 4) is curved, suggesting that in addition to being a first-generation product acetaldehyde is also formed from secondary reactions of other first-generation products (formation from propanal[1,31] probably being most important). The acetaldehyde formation yield during the initial stages of the reaction, obtained from a second-order regression, is listed in Table 3 and is taken to be the yield of acetaldehyde as a first-generation product.

API-MS analyses of irradiated $CH_3ONO/NO/3,4$-diethylhexane/air mixtures in the positive ion mode showed the presence of significant ion peaks at 87, 105, 155, 171, 173, and 306 u

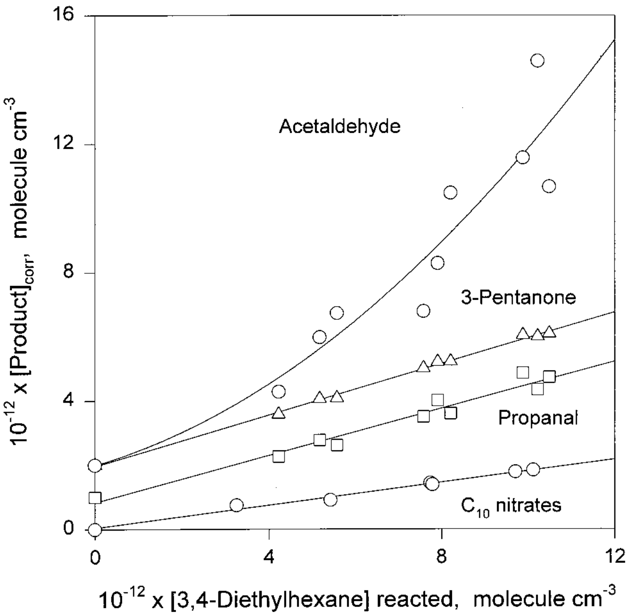

Figure 4. Plots of the amounts of C_{10} alkyl nitrates (total), propanal, 3-pentanone and acetaldehyde formed, corrected for secondary reactions with OH radicals (see text), against the amounts of 3,4-diethylhexane reacted with the OH radical. The data for propanal, 3-pentanone and acetaldehyde have been displaced vertically by 1.0 × 10^{12} molecules cm^{-3}, 2.0 × 10^{12} molecules cm^{-3}, and 2.0 × 10^{12} molecules cm^{-3}, respectively, for clarity. The line through the acetaldehyde data is from a second-order regression (see text).

TABLE 3: Products and Their Fractional Molar Yields from the Gas-Phase Reaction of OH Radicals with 3,4-Diethylhexane in the Presence of NO

product	GC−FID analyses[a]	API-MS analyses
acetaldehyde	0.40[b]	
propanal	0.37 ± 0.06	observed[c]
3-pentanone	0.40 ± 0.04	observed[c]
3-pentyl nitrate	0.023 ± 0.011	
$CH_3CH(ONO_2)CH(C_2H_5)$-$CH(C_2H_5)_2$	0.145 ± 0.026	
$(CH_3CH_2)_2C(ONO_2)CH$-$(C_2H_5)_2$	0.032 ± 0.008	
total C_{10} alkyl nitrates	0.177 ± 0.032	
hydroxycarbonyls		observed (MW 172)[c] observed, yield ~0.11[d]
hydroxynitrates		observed (MW 191, 219)[c] observed, yield ~0.017[e]

[a] Indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC−FID response factors for diethylhexane and products of ±5% each (and for the alkyl nitrates relative to that for 3,4-diethylhexane of ±15%). [b] Yield cited is the initial slope obtained from a second-order regression (see text). [c] Positive ion mode. [d] Negative ion mode as NO_2^- adducts. Weak ion peaks attributed to C_5-, C_6-, C_8-, C_9-, and C_{10}-hydroxycarbonyls observed; yield is the sum of these hydroxycarbonyls. [e] Negative ion mode as NO_2^- adducts. C_5-, C_8-, and C_{10}-hydroxynitrates observed with average ratios 0.25: 0.18: 1.00; yield is the sum of these hydroxynitrates.

(Figure 5A), with less intense ion peaks at 203, 238, 278, and 439 u. API-MS/MS "product ion" and "precursor ion" spectra indicated that these ion peaks in the API-MS spectra were due to products of molecular weight 58, 86, 172, 191, and 219, with the observed ion peaks at 87 and 105 being the $[M+H]^+$ and $[M+H_3O]^+$ ions of the molecular weight 86 product (attributed to 3-pentanone), the ion peaks at 155, 171 and 173 being the $[M+H-H_2O]^+$, $[M+H-H_2]^+$ and $[M+H]^+$, respectively, of the molecular weight 172 product (and that at 173 u also the protonated dimer of the molecular weight 86 product), the 278 u ion peak being a protonated heterodimer of the molecular weight 86 and 191 products, the 238 u ion peak being the $[M+H_3O]^+$ of the molecular weight 219 product, the 306 u ion peak being the protonated heterodimer of the molecular weight 219 and 86 products, and the 439 u ion peak being the protonated dimer of the molecular weight 219 species. The presence of propanal, which was quantified by GC−FID (Table 3), as a product in the API-MS analyses was determined by MS/MS analysis of the small 203 u ion peak which is attributed to a protonated heterodimer of two molecules of propanal plus 3-pentanone. Analogous to the *n*-decane reaction system, the molecular weight 172 and 219 products are attributed to a hydroxycarbonyl of formula $C_{10}H_{19}(OH)(O)$ and a hydroxynitrate of formula $C_{10}H_{20}(OH)(ONO_2)$. Thus, the only major products not observed in the positive ion mode were acetaldehyde and the C_{10} alkyl nitrates quantified by GC−FID (see Table 3).

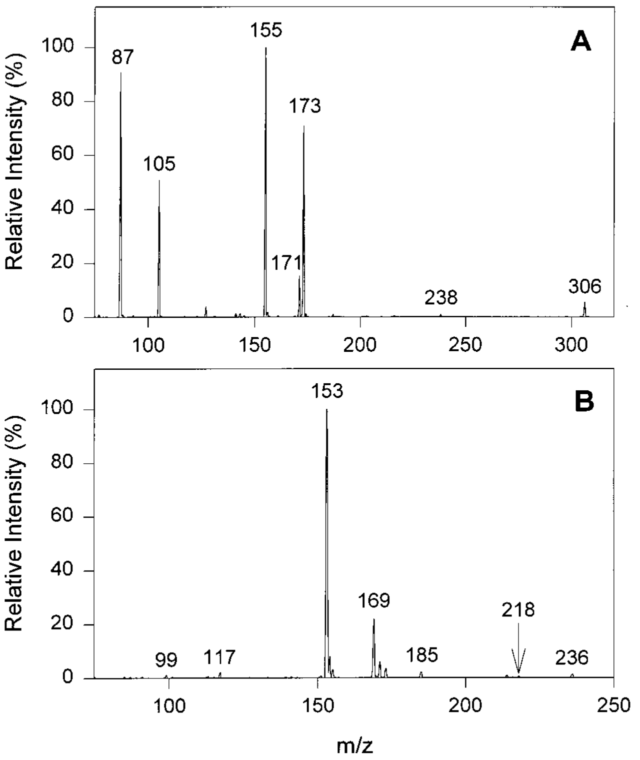

Figure 5. API-MS positive ion mode spectra of (A) an irradiated CH_3ONO/NO/3,4-diethylhexane/air mixture and (B) an irradiated CH_3ONO/NO/*n*-butylcyclohexane/air mixture, with protonation by $H_3O^+(H_2O)_n$ ions. See text for assignments of the observed ion peaks.

In the negative ion mode, API-MS spectra of irradiated CH_3ONO/NO/3,4-diethylhexane/air mixtures after addition of NO_2 showed the presence of significant ion peaks at 195, 237, 265, and 281 u, with the 195, 237, and 265 u ion peaks being attributed to NO_2^- adducts of molecular weight 149, 191, and 219 species, and with the 281 u ion peak potentially being an NO_3^- adduct of the molecular weight 219 species. As noted above, the negative ion mode is extremely sensitive to hydroxynitrates[15] and the molecular weight 149 and 191 species are attributed to C_5- and C_8-hydroxynitrates. It should be noted that the ion peaks arising from hydroxycarbonyls were of low intensity in the negative ion mode, despite the fact that they were prominent in the positive ion mode (Figure 5A). Experiments were carried out with 5-hydroxy-2-pentanone being added as the internal standard after the irradiation, and the yield of hydroxycarbonyls from the 3,4-diethylhexane reaction is given in Table 3. In two of these experiments, $CH_3CH(OH)CH$-

$(ONO_2)CH_3$ was formed in situ from the reaction of the OH radical with *cis*-2-butene[22,23] and used as an internal standard for hydroxyalkyl nitrate quantification. The hydroxynitrate formation yield resulting from these experiments are also given in Table 3.

3,4-Diethylhexane Reaction Mechanism. It is calculated that the fractions of the initial OH radical reaction proceeding by H atom abstraction from the CH_3, CH_2, and CH groups are 5.4%, 36.8% and 57.8%, respectively,[27,28] noting that this prediction is likely to be in error because the measured rate constant for 3,4-diethylhexane is 40% lower than the estimated value (Table 1). Reactions 2 and 3 then lead to the formation of primary, secondary and tertiary C_{10} alkyl nitrates $O_2NOCH_2CH_2CH(CH_2CH_3)CH(CH_2CH_3)_2$, $CH_3CH(ONO_2)CH(CH_2CH_3)CH(CH_2CH_3)_2$, and $(CH_3CH_2)_2C(ONO_2)CH(CH_2CH_3)_2$ [of molecular weight 203], or NO_2 plus the alkoxy radicals $(CH_3CH_2)_2CHCH(CH_2CH_3)CH_2CH_2\dot{O}$, $CH_3CH(\dot{O})CH(CH_2CH_3)CH(CH_2CH_3)_2$, and $(CH_3CH_2)_2C(\dot{O})CH(CH_2CH_3)_2$.

It is estimated[2,3,31] that decomposition of the $(CH_3CH_2)_2C(\dot{O})CH(CH_2CH_3)_2$ radical

$$(CH_3CH_2)_2C(\dot{O})CH(CH_2CH_3)_2 \rightarrow CH_3CH_2C(O)CH_2CH_3 + CH_3CH_2\dot{C}HCH_2CH_3 \tag{10}$$

dominates over isomerization at 298 K by a factor of 10^2, with the 3-pentyl radical formed from the OH radical-initiated reaction of *n*-pentane in the presence of NO reacting to form 3-pentyl nitrate (12.6%), 3-pentanone (52%), and acetaldehyde plus propanal (35%).[11,15]

It is also estimated[2,3,31] that the $CH_3CH(\dot{O})CH(CH_2CH_3)CH(CH_2CH_3)_2$ radical will primarily undergo isomerization ($4.2 \times 10^6\ s^{-1}$) and decomposition ($2.2 \times 10^6\ s^{-1}$). The isomerization pathway is expected to form mainly the C_{10} hydroxycarbonyl $CH_3C(O)CH(CH_2CH_3)CH(CH_2CH_3)CH(OH)CH_3$ (see results of the *n*-decane reaction system, above). The alkoxy radical $CH_3CH_2CH(\dot{O})CH(CH_2CH_3)_2$ formed from the decomposition reaction 11

$$CH_3CH(\dot{O})CH(CH_2CH_3)CH(CH_2CH_3)_2 \rightarrow CH_3CHO + CH_3CH_2\dot{C}HCH(CH_2CH_3)_2 \tag{11}$$

is predicted[2,3,33] to react mainly (85%) via decomposition [reaction 12] to yield propanal and the 3-pentyl radical (which as noted above reacts to form 3-pentyl nitrate, acetaldehyde, propanal and 3-pentanone[11,15]), and by isomerization [reaction 13]

$$CH_3CH_2CH(\dot{O})CH(CH_2CH_3)_2 \rightarrow CH_3CH_2CHO + CH_3CH_2\dot{C}HCH_2CH_3 \tag{12}$$

$$CH_3CH_2CH(\dot{O})CH(CH_2CH_3)_2 \rightarrow CH_3CH_2CH(OH)CH(CH_2CH_3)CH_2\dot{C}H_2 \tag{13}$$

The hydroxyalkyl radical formed in reaction 13 is anticipated[2,3,31] to react by a sequence of reactions, including a second isomerization, to form the C_8-hydroxycarbonyl $CH_3CH_2C(O)CH(CH_2CH_3)CH_2CH_2OH$ and the C_8-hydroxynitrate $CH_3CH_2CH(OH)CH(CH_2CH_3)CH_2CH_2ONO_2$.

The primary alkoxy radical $(CH_3CH_2)_2CHCH(CH_2CH_3)CH_2CH_2\dot{O}$ is predicted[2,3,31] to undergo almost exclusively isomerization leading to (after reaction of the resulting hydroxyalkyl radical with O_2 and then NO) the $(CH_3CH_2)_2C(\dot{O})CH(CH_2CH_3)CH_2CH_2OH$ radical, which is predicted to decompose [reaction 14] (84% of the time) rather than undergo another isomerization to ultimately form $(CH_3CH_2)_2C(OH)CH(CH_2CH_3)CH_2CHO$

$$(CH_3CH_2)_2C(\dot{O})CH(CH_2CH_3)CH_2CH_2OH \rightarrow CH_3CH_2C(O)CH_2CH_3 + HOCH_2CH_2\dot{C}HCH_2CH_3 \tag{14}$$

Further reactions of the 1-hydroxy-3-pentyl radical are expected to lead to the formation of the C_5-hydroxynitrate $HOCH_2CH_2CH(ONO_2)CH_2CH_3$, 1-hydroxy-3-pentanone, and propanal plus glycolaldehyde or HCHO + HCHO.

Our product data are in reasonable accord with these expectations. On the basis of our measured 3-pentanone yield, and taking into account formation of the tertiary nitrate and assuming formation of 3-pentanone only from reaction 10, then H-atom abstraction from the tertiary C−H bonds of 3,4-diethylhexane must account for <47% of the overall OH radical reaction. If the $CH_3CH_2CH(\dot{O})CH(CH_2CH_3)_2$ radical only undergoes decomposition and forms 1.52 molecules of 3-pentanone (see above), then H-atom abstraction from the tertiary C−H bonds of 3,4-diethylhexane must account for <33% of the overall OH radical reaction, significantly lower than the 58% predicted.[27,28] Using our measured rate constant and assuming that the rates of H-atom abstraction from the primary and secondary C−H bonds in 3,4-diethylhexane are those predicted,[27,28] then the percentages of H-atom abstraction from the primary, secondary and tertiary C−H bonds are 9%, 62% and 29%, respectively. Taking into account our measured C_{10} alkyl nitrate yields (Table 3), then the percentages of the C_{10} alkoxy radicals formed are 9% $(CH_3CH_2)_2CHCH(CH_2CH_3)CH_2CH_2\dot{O}$ radicals, 47% $CH_3CH(\dot{O})CH(CH_2CH_3)CH(CH_2CH_3)_2$ radicals, and 26% $(CH_3CH_2)_2C(\dot{O})CH(CH_2CH_3)_2$ radicals. The subsequent reactions of these alkoxy radicals are predicted[2,3,11,31] to lead to 54% 3-pentanone, 31% propanal, 30% acetaldehyde and 5.2% 3-pentyl nitrate, compared to our measured 3-pentanone, propanal, acetaldehyde and 3-pentyl nitrate yields of 40 ± 4%, 37 ± 6%, ∼40%, and 2.3 ± 1.1%, respectively. Analogous to reactions of the $HOCH_2CH_2\dot{O}$ radical formed from the exothermic $HOCH_2CH_2O\dot{O}$ + NO reaction, where decomposition is enhanced over that for $HOCH_2CH_2\dot{O}$ radicals formed from the approximately thermoneutral peroxy + peroxy radical reaction,[32] it is possible that decomposition of the $(CH_3CH_2)_2C(\dot{O})CH(CH_2CH_3)_2$ radical to 3-pentanone plus 3-pentyl radical (which is estimated to be slightly exothermic[33−35]) leads to some of the excess energy residing in the 3-pentyl radical, and ultimately leading to (a) a lower yield of 3-pentyl nitrate from the 3-pentyl peroxy + NO reaction and (b) the 3-pentoxy radical formed in the 3-pentyl peroxy + NO reaction preferentially decomposing to form acetaldehyde plus propanal rather than reacting with O_2 to form 3-pentanone. If this is the case, then the predicted 3-pentanone, propanal, acetaldehyde, and 3-pentyl nitrate yields are 41%, 44−48%, 43−47%, and 1.8−5.2%, respectively (with the ranges for propanal, acetaldehyde and 3-pentyl nitrate depending on the amount of 3-pentyl nitrate formed from the $(CH_3CH_2)_2C(\dot{O})CH(CH_2CH_3)_2$ radical reactions). The resulting good agreement with our measured 3-pentanone, propanal, acetaldehyde and 3-pentyl nitrate yields suggests that the 3-pentoxy radical formed from the $(CH_3CH_2)_2C(\dot{O})CH(CH_2CH_3)_2$ radical preferentially decomposes rather than reacting with O_2.

Using these percentages of H-atom abstraction from the secondary and tertiary C−H bonds in 3,4-diethylhexane of 62% and 29%, respectively, the formation yields of secondary and tertiary C_{10} alkyl nitrates from their precursor $R\dot{O}_2$ radicals are ∼0.24 and ∼0.11, respectively, consistent with an expected

TABLE 4: Products and Their Fractional Molar Yields from the Gas-Phase Reaction of OH Radicals with *n*-Butylcyclohexane in the Presence of NO

product	GC−FID analyses[a]	API-MS analyses
propanal	≤0.05	
butanal	0.072 ± 0.009	observed[b]
cyclohexanone	0.049 ± 0.007	observed[b]
total C_{10} alkyl nitrates	0.19 ± 0.06	
total hydroxycarbonyls		observed (MW 170)[b] observed, yield ~0.37[c]
total hydroxynitrates		observed (MW 217)[b] yield ~0.023[d]

[a] Indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC−FID response factors for *n*-butylcyclohexane and products of ±5% each (and for the alkyl nitrates relative to that for *n*-butylcyclohexane of ±15%). [b] Positive ion mode. [c] Negative ion mode as NO_2^- adducts. Ion peaks attributed to C_9- and C_{10}-hydroxycarbonyls observed with average ratio 0.18: 1.00; yield is the sum of these hydroxycarbonyls. [d] Negative ion mode as NO_2^- adducts. C_{10}-hydroxynitrate(s) and, possibly, C_{10}-hydroxycarbonylnitrates(s) observed; yield is the sum of the ion peaks at 263 and 279 u.

formation yield of $CH_3CH(ONO_2)CH(CH_2CH_3)CH(CH_2CH_3)_2$ from its precursor $C_{10}H_{21}\dot{O}_2$ radical of ~27%[15] and a significantly lower yield of $(CH_3CH_2)_2C(ONO_2)CH(CH_2CH_3)_2$ from its precursor tertiary $C_{10}H_{21}\dot{O}_2$ radical.[16] The products identified and quantified by gas chromatography account for ~60% of the reaction pathways. The majority of the remaining products are predicted to be C_5-, C_8-, and C_{10}-hydroxycarbonyls and hydroxynitrates, which our API-MS analyses indicate account for an additional ~13% (uncertain to a factor of 2−3) of the overall products.

***n*-Butylcyclohexane.** GC−FID and GC-MS analyses of irradiated CH_3ONO/NO/*n*-butylcyclohexane/air mixtures showed the formation of butanal, cyclohexanone, and seven closely eluting C_{10}-alkyl nitrates. The GC analyses showed no evidence for the formation of propanal. Least-squares analyses of plots of the amounts of products formed, corrected for secondary reactions, against the amounts of *n*-butylcyclohexane reacted lead to the product formation yields given in Table 4.

API-MS analysis of irradiated CH_3ONO/NO/*n*-butylcyclohexane/air mixtures in the positive ion mode showed the presence of product ion peaks at 99, 117, 153, 169, 171, 185, 218, and 236 u (Figure 5B). API-MS/MS "product ion" and "precursor ion" spectra indicated that the observed ion peaks at 99 and 117 u were the $[M+H]^+$ and $[M+H_3O]^+$ ions of a molecular weight 98 product (attributed to cyclohexanone), the ion peaks at 153, 169, and 171 were the $[M+H-H_2O]^+$, $[M+H-H_2]^+$ and $[M+H]^+$, respectively, of a molecular weight 170 product, and the 218 and 236 u ion peaks were, respectively, the $[M+H]^+$ and $[M+H_3O]^+$ of a molecular weight 217 product. An API-MS/MS "product ion" spectrum of the 218 u ion peak showed the presence of an intense fragment at 46 u (NO_2^+), thereby indicating that the molecular weight 217 product is an organic nitrate. As discussed below, the molecular weight 170 product is attributed to a hydroxycarbonyl and/or dicarbonyl of formula $C_{10}H_{18}O_2$, whereas the molecular weight 217 product is attributed to a hydroxynitrate and/or carbonyl-nitrate of formula $C_{10}H_{19}O(ONO_2)$.

API-MS spectra of irradiated CH_3ONO/NO/*n*-butylcyclohexane/air mixtures in the negative ion mode after addition of NO_2 showed the presence of significant ion peaks at 216, 263, and 279 u, with the 216 and 263 u ion peaks being attributed to NO_2^- adducts of molecular weight 170 and 217 species, and with the 279 u ion peak potentially being an NO_3^- adduct of the molecular weight 217 species or an NO_2^- adduct of a molecular weight 233 dihydroxynitrate (see below). Experiments were carried out with 5-hydroxy-2-pentanone added as the internal standard after the irradiation, and the yield of hydroxycarbonyls from the *n*-butylcyclohexane reaction is given in Table 4. In two of these experiments, $CH_3CH(OH)CH(ONO_2)CH_3$ was formed in situ from the reaction of the OH radical with *cis*-2-butene[22,23] and used as an internal standard for hydroxyalkyl nitrate quantification. The hydroxynitrate formation yield resulting from these experiments is also given in Table 4.

***n*-Butylcyclohexane Reaction Mechanism.** It is estimated[27,28] that the percentages of the OH radical reaction proceeding by H atom abstraction are: from the CH_2 groups, 9.5% each (except for the CH_2 group adjacent to the CH_3 group in the *n*-butyl side-chain which is estimated to be 7.8%); from the tertiary CH group, 24%; and from the CH_3 group, 1.1%. As discussed above for *n*-decane and 3,4-diethylhexane, the initially formed alkyl radicals will add O_2 and then react with NO to form C_{10} alkyl nitrates (of molecular weight 201) or C_{10} alkoxy radicals plus NO_2. Using the estimation method of Aschmann and Atkinson,[31] it is predicted that the alkoxy radicals $CH_3CH(\dot{O})CH_2CH_2$-cyc-C_6H_{11}, $CH_3CH_2CH(\dot{O})CH_2$-cyc-C_6H_{11}, and 1-butyl-1-cyclohexoxy will dominantly isomerize, to ultimately form molecular weight 170 hydroxycarbonyls. In contrast, the $CH_3CH_2CH_2CH(\dot{O})$-cyc-C_6H_{11} radical is predicted to decompose [reaction 15]

$$CH_3CH_2CH_2CH(\dot{O})\text{-cyc-}C_6H_{11} \rightarrow CH_3CH_2CH_2CHO + \text{cyc-}\dot{C}_6H_{11} \quad (15)$$

with the cyclohexyl radical reacting further to form cyclohexyl nitrate (16%) and cyclohexanone (32%), plus a number of other products including $HC(O)CH_2CH_2CH_2CH_2CHO$ and $HC(O)CH_2CH(OH)CH_2CH_2CHO$.[12−14] The predicted yields of butanal and cyclohexanone are therefore 7.7% and 2.5%, respectively, assuming an alkyl nitrate yield of 19% from the secondary $C_{10}H_{19}\dot{O}_2$ radical. This predicted butanal yield is close to that measured (7.2 ± 0.9%), whereas the measured cyclohexanone yield of 4.9 ± 0.7% is a factor of 2 higher than the predicted value, implying other sources of cyclohexanone. These could include formation of cyclohexanone from the predicted dominant isomerization of the $\dot{O}CH_2CH_2CH_2CH_2$-cyc-C_6H_{11} radical to form the $HOCH_2CH_2CH_2CH(\dot{O})$-cyc-$C_6H_{11}$ alkoxy radical, which can either decompose [to $HOCH_2CH_2CH_2CHO$ plus cyclohexyl radical] or isomerize, with these processes being estimated to be competitive (3.8×10^6 s^{-1} and 9×10^6 s^{-1} at 298 K, respectively), and with the cyclohexyl radical forming in part cyclohexanone (see above). A second minor pathway to cyclohexanone involves decomposition of the 1-butyl-1-cyclohexoxy radical [reaction 16], predicted to be a minor pathway compared to isomerization (2.6×10^4 s^{-1} and 2×10^6 s^{-1} at 298 K, respectively)

$$\text{1-butyl-1-cyclohexoxy} \rightarrow \text{cyclohexanone} + CH_3CH_2CH_2\dot{C}H_2 \quad (16)$$

with the butyl radical forming butanal (~23%) and 4-hydroxybutanal (~77%).[2,11]

The 2-butyl-1-cyclohexoxy and 3-butyl-1-cyclohexoxy radicals may dominantly isomerize, depending on whether the conformation of the six-membered transition state is favorable. Otherwise, as for the 4-butyl-1-cyclohexoxy radical, they will react with O_2 and decompose, with decomposition being expected to be important[12] and with (by analogy with the cyclohexane system[12]) the resulting ring-opened radicals reacting to form carbonyl-nitrates of molecular weight 217, hydroxy-

TABLE 5: Product Formation Yields from Reactions of the OH Radical with a Series of C_5-C_{10} Alkanes Studied in This Laboratory, in the Presence of NO (This Work and Reference 15)

	yield (%)			
alkane	carbonyls[a]	alkyl nitrates	hydroxy-carbonyls	hydroxy-nitrates
n-pentane	47	10.5	36	2.6
n-hexane	10	14.1	53	4.6
n-heptane	≤1	17.8	46	4.7
n-octane	≤1	22.6	27	5.4
n-decane		22.6	22	2.4
3,4-diethylhexane	∼40	18	11	1.7
n-butylcyclohexane	7	19	37	2.3

[a] From decomposition or reaction with O_2 of the alkoxy radicals.[3,11] The cited yields account for the formation of two carbonyls as coproducts in many instances and hence the cited yields refer to the reaction pathways.

carbonylnitrates of molecular weight 233, hydroxydicarbonyls of molecular weight 186, and, to a lesser extent, dicarbonyls of molecular weight 170. As mentioned above, ion peaks attributed to products of molecular weight 170, 217 and, possibly, 233 were observed in the API-MS analyses. In the case of the hydroxydicarbonyls of molecular weight 186, it is possible that the major ion peak observed from this product in the positive ion mode was the $[M+H-H_2O]^+$ at 169 u, which is isobaric with the $[M+H-H_2]^+$ of the molecular weight 170 hydroxycarbonyl(s), and that the observed 185 u ion peak (Figure 5B) is the $[M+H-H_2]^+$ of this hydroxydicarbonyl.

Our product yield data given in Table 4 (assuming that butanal and cyclohexanone are formed as coproducts) account for 65% of the reaction products and pathways (and taking the uncertainties into account), with a range of ∼40−110%.

Atmospheric Implications. Combining our room-temperature rate constants for the reactions of OH radicals with *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane with a 24-hr average OH radical concentration of 1.0×10^6 molecule cm^{-3} (the global tropospheric average)[36,37] leads to tropospheric lifetimes of 0.9 days, 1.6 days and 0.7 days for *n*-decane, 3,4-diethylhexane, and *n*-butylcyclohexane, respectively. The products observed and quantified show that the detailed reactions after the initial H-atom abstraction depend on the structure of the alkane, with the alkoxy radicals produced from *n*-decane and *n*-butylcyclohexane undergoing largely isomerization and leading to hydroxycarbonyl formation, whereas the alkoxy radicals formed from 3,4-diethylhexane also decompose to a significant or dominant extent, thereby leading to volatile products which can be readily analyzed by gas chromatography. As shown in Table 5 for a series of C_5-C_{10} alkanes for which hydroxycarbonyl and hydroxynitrate yields are available (this work and ref 15), the major reaction products of several alkanes are now known and a significant fraction 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 hydroxynitrates. The estimation method proposed by Atkinson[2,3] and revised by Aschmann and Atkinson[31] appears to be useful in that its quantitative predictions concerning the products formed and their yields are in generally good agreement with our experimental observations.

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