

**ATMOSPHERIC CHEMISTRY OF SELECTED LINEAR, BRANCHED  
AND CYCLIC C<sub>10</sub> ALKANE COMPONENTS OF MINERAL SPIRITS**

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## Abstract

Ozone pollution in urban areas is the result of the reactions of volatile organic compounds, including alkanes, with oxides of nitrogen under the influence of sunlight. Alkanes are significant components of gasoline and diesel fuels and of vehicle exhaust, and alkanes containing 9-13 carbon atoms are important constituents of mineral spirits. In the atmosphere, alkanes react with the hydroxyl (OH) radical to form a suite of products, certain of which are presently difficult to identify and quantify. Of particular interest because of their potential impact on ozone production is the formation of organic nitrates from the OH radical-initiated reactions of alkanes in the presence of  $\text{NO}_x$ . Because  $\text{NO}_2$  which would otherwise be photolyzed to form ozone is sequestered in the organic nitrates, accurate measurements of the amounts of organic nitrates formed, including hydroxyalkyl nitrates, is critical to predictions of ozone formation from alkane photooxidations. The formation yields of alkyl nitrates from *n*-hexane, *n*-heptane and *n*-octane were measured to be  $0.141 \pm 0.020$ ,  $0.178 \pm 0.024$ , and  $0.226 \pm 0.032$ , respectively. These alkyl nitrate yields are ~35% lower than previous data reported from this laboratory in the early 1980's. Through the use of negative ion atmospheric pressure chemical ionization mass spectrometry, 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. The yields of the hydroxycarbonyl and hydroxynitrate products were quantified relative to internal standards of similar chemical structure.

We then investigated the atmospheric chemistry of three representative linear, branched and cyclic  $\text{C}_{10}$  alkanes, *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane. Using a relative rate method, rate constants for reactions of the OH radical with *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane (in units of  $10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) were measured to be  $12.5 \pm 0.4$ ,  $7.43 \pm 0.48$  and  $15.8 \pm 0.6$ , 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, hydroxycarbonyls and hydroxynitrates from the 3,4-diethylhexane reaction; and butanal, cyclohexanone, hydroxycarbonyls and hydroxynitrates from the *n*-butylcyclohexane reaction. These observed gas-phase products account for a significant fraction of the total products.

## Executive Summary

### Background

Ozone pollution in urban areas is the result of the reactions of volatile organic compounds, including alkanes, with oxides of nitrogen under the influence of sunlight. Alkanes are significant components of gasoline and diesel fuels and of vehicle exhaust, and alkanes containing 9-13 carbon atoms are important constituents of mineral spirits. In the atmosphere, alkanes react with the hydroxyl (OH) radical to form a suite of products, certain of which are presently difficult to identify and quantify. Of particular interest because of their potential impact on ozone production is the formation of organic nitrates from the OH radical-initiated reactions of alkanes in the presence of NO<sub>x</sub>. Because NO<sub>2</sub> which would otherwise be photolyzed to form ozone is sequestered in the organic nitrates, accurate measurements of the amounts of organic nitrates formed, including hydroxyalkyl nitrates, is critical to predictions of ozone formation from alkane photooxidations.

### Methods

In this two-year contract, we investigated the products of the gas-phase reactions of OH radicals with several alkanes using gas chromatography with flame ionization detection (GC-FID) and combined gas chromatography-mass spectrometry (GC-MS) to identify and quantify products including alkyl nitrates, and *in situ* atmospheric pressure ionization mass spectrometry (API-MS) to identify hydroxycarbonyl and hydroxynitrate products. Using negative ion API-MS with the addition of pentafluorobenzyl alcohol as a chemical ionization reagent, hydroxyalkyl nitrate products were identified from the *n*-pentane, *n*-heptane and *n*-octane reactions for the first time. The addition of NO<sub>2</sub> to the chamber reaction mixture post-reaction to form [NO<sub>2</sub>-M]<sup>-</sup> 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 determined.

### Results

We investigated the 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 and determined the formation yields for the sum of the isomeric alkyl nitrates from *n*-hexane, *n*-heptane and *n*-octane as 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 1980's. Using negative ion API-MS 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. Although the uncertainties in the measured concentrations of hydroxycarbonyls and hydroxynitrates is estimated to be in the range of a factor of 2-3 (and probably increasing with increasing size of the alkane), our data show that hydroxycarbonyl formation from the C<sub>5</sub>-C<sub>8</sub> *n*-alkanes is very important, accounting for the majority of the reaction products. The measured hydroxynitrate formation yields from the C<sub>5</sub>-C<sub>8</sub> *n*-alkanes are consistently ~25% of the corresponding alkyl

nitrate yields.

We then investigated the atmospheric chemistry of three representative linear, branched and cyclic C<sub>10</sub> alkanes, *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane. Using a relative rate method, rate constants for reactions of the OH radical with *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane were measured to be (in units of 10<sup>12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) 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, hydroxycarbonyls and hydroxynitrates from the 3,4-diethylhexane reaction; and butanal, cyclohexanone, hydroxycarbonyls and hydroxynitrates from the *n*-butylcyclohexane reaction. The products identified from the OH radical-initiated reactions of *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane in the presence of NO show that the detailed reactions subsequent to 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, while the alkoxy radicals formed from 3,4-diethylhexane also decomposed to a significant or dominant extent leading to volatile products.

## Conclusions

Our alkyl nitrate, hydroxyalkyl nitrate and hydroxycarbonyl formation yields, combined with the literature carbonyl yields arising from alkoxy radical decomposition and reaction with O<sub>2</sub>, account for ~95%, ~80%, ~70%, ~55%, ~45-50%, ~70% and ~65% of the products formed from the OH radical-initiated reactions of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane (in the presence of NO), respectively, with uncertainties of approximately a factor of 1.5 in each case. We can therefore now account for most of the reaction products formed from these alkanes, and hydroxycarbonyl formation accounts for a significant fraction of these products. Hydroxyalkyl nitrate formation accounts for a few percent of the overall reaction products, and is 10-25% of the corresponding alkyl nitrate yields. Thus significant fractions of the atmospheric reaction products of ≥C<sub>5</sub> *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. The experimental data obtained during this contract have now been implemented into a detailed chemical mechanism for ozone formation.

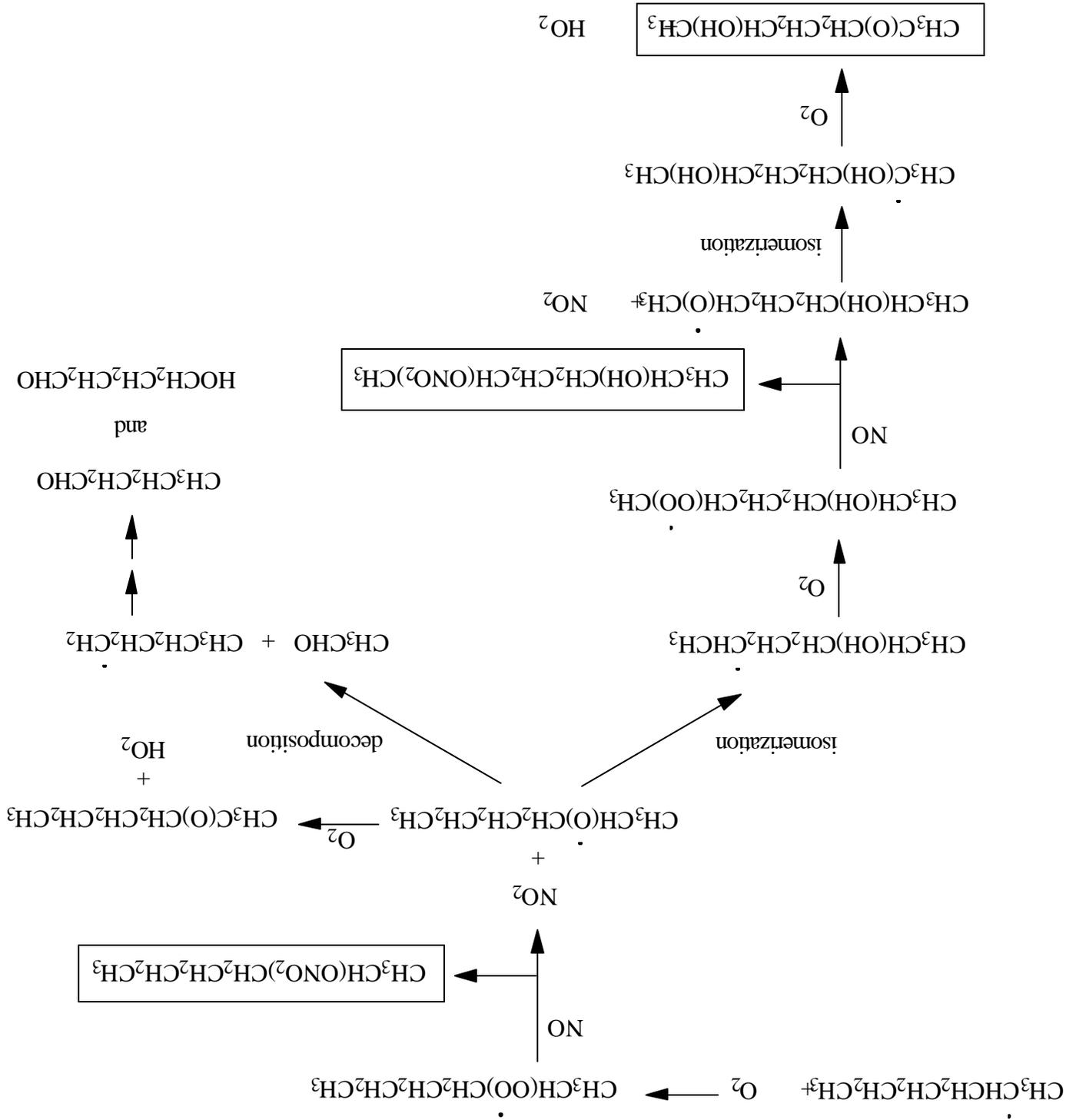
## Introduction

Alkanes are significant components of gasoline and diesel fuels and of vehicle exhaust, and alkanes containing 9-13 carbon atoms are important constituents of mineral spirits. In the troposphere, alkanes present in the gas phase react mainly with the OH radical (Atkinson, 1997a, 2000a) to form an alkyl radical.

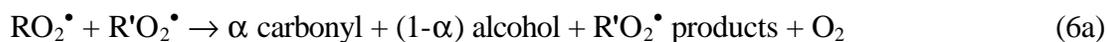
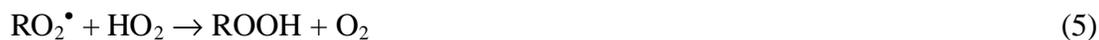
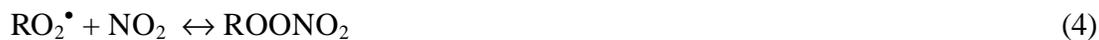
$$\text{OH} + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}^\bullet$$

Alkyl radicals react rapidly with  $\text{O}_2$  in the troposphere to form alkyl peroxy ( $\text{RO}_2^\bullet$ ) radicals, which then react with  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HO}_2$  radicals or with other organic peroxy ( $\text{R}'\text{O}_2^\bullet$ ) radicals (Atkinson, 1997a,

(1)



2000a).



In the presence of NO at mixing ratios  $\geq 10$ -30 parts-per-trillion, peroxy radical reactions with NO [reaction (3)] will dominate (Logan, 1985) and the products of the alkyl peroxy radical reactions with NO are the corresponding alkoxy radical plus  $NO_2$  or the alkyl nitrate,  $RONO_2$  (Atkinson, 1997a, 2000a), as illustrated in Scheme 1 for the 2-hexyl radical formed from *n*-hexane.

The alkoxy radicals formed in reactions (3b) and (6b) then react with  $O_2$ , decompose by C-C bond scission, or isomerize through a 6-membered ring transition state (Atkinson, 1997a,b, 2000a), 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) and (3b) and Scheme 1, leading to the formation of a 1,4-hydroxyalkoxy radical plus  $NO_2$  or a 1,4-hydroxyalkyl nitrate. The 1,4-hydroxyalkoxy radical is expected to undergo a second (rapid) isomerization, leading to the formation of a 1,4-hydroxycarbonyl (Atkinson, 1997a,b, 2000a).

Scheme 1

As shown in reactions (3a) and (3b), the reactions of  $\text{RO}_2^\bullet$  radicals with NO lead to the formation of the corresponding alkoxy radical plus  $\text{NO}_2$  or an organic nitrate,  $\text{RONO}_2$ . To date, alkyl nitrate yields have been measured from the reactions of the  $\text{C}_2$  through  $\text{C}_8$  *n*-alkanes, cyclohexane, and from the reactions of four branched alkanes (Darnall *et al.*, 1976; Tagaki *et al.*, 1981; Atkinson *et al.*, 1982a, 1983, 1984, 1987, 1995a; Harris and Kerr, 1989; Carter and Atkinson, 1989; Platz *et al.*, 1999; Orlando *et al.*, 2000). The measured alkyl nitrate yields increase with increasing pressure and with decreasing temperature (Carter and Atkinson, 1989; Atkinson, 1994, 1997a). For the *n*-alkane series the alkyl nitrate yields increase with increasing carbon number, with an octyl nitrate yield from the *n*-octane reaction of ~30% (Carter and Atkinson, 1989; Atkinson, 1994, 1997a). The few available data indicate that the alkyl nitrate yields from primary and tertiary alkyl peroxy groups ( $\text{RCH}_2\text{O}_2^\bullet$  and  $\text{R}_3\text{CO}_2^\bullet$ , respectively) are lower than the alkyl nitrate yields from secondary alkyl peroxy,  $\text{R}_2\text{CHO}_2^\bullet$ , radicals (Carter and Atkinson, 1989; Atkinson, 1994, 1997a). Prior to the results of the present study, the formation of hydroxyalkyl nitrates from the OH radical-initiated reactions of alkanes, arising subsequent to alkoxy radical isomerization (Scheme 1), had been observed only from *n*-hexane (Eberhard *et al.*, 1995) and 2,2,4-trimethylpentane (Aschmann *et al.*, 2001), and then-current chemical mechanisms for ozone formation from alkanes assumed a zero formation yield of hydroxynitrates from the reactions of hydroxyalkyl peroxy radicals with NO (Carter, 1990).

In terms of ozone formation from the OH radical-initiated reactions of alkanes, the formation of alkyl nitrates leads to the removal of  $\text{NO}_2$  which would otherwise photolyze to form  $\text{O}_3$  (and also results in the removal of radicals, reducing the reactivity of the entire air mass). In addition, the three alkoxy radical reaction pathways (see Scheme 1) result in differing amounts of NO-to- $\text{NO}_2$  conversion and hence of  $\text{O}_3$  formation. Furthermore, as shown above the isomerization reaction can lead to the formation of hydroxynitrates from the reaction of the hydroxyalkyl peroxy radicals with NO (Scheme 1). Experimental observations of hydroxynitrate formation from *n*-hexane and 2,2,4-trimethylpentane were therefore inconsistent with then-current chemical mechanisms for alkane photooxidations (Carter, 1990), indicating that there were errors in the chemical mechanisms which needed to be elucidated before reliable predictions of ozone-forming potentials for mineral spirits could be made from computer modeling studies.

Until the present study, product studies have focussed on the smaller alkanes such as *n*-butane, *n*-pentane and *n*-hexane (see Atkinson, 1997a). Eberhard *et al.* (1995) used a derivatization method followed by chromatography to investigate the products formed from *n*-hexane, and observed the formation of the hydroxycarbonyls expected after isomerization of the intermediate 2- and 3-hexoxy radicals. We have previously used *in situ* atmospheric pressure ionization tandem mass spectrometry (API-MS/MS) to semi-quantitatively investigate the products formed from the OH radical-initiated reactions of *n*-butane through *n*-octane and of *n*-pentane- $\text{d}_{12}$  through *n*-octane- $\text{d}_{18}$  in the presence of NO (Kwok *et al.*, 1996), and observed the formation of the hydroxycarbonyls and carbonyls expected after isomerization and decomposition, respectively, of the intermediate alkoxy radicals. The data obtained indicate that isomerization dominates over decomposition for the alkoxy radicals formed from *n*-hexane through *n*-octane (Kwok *et al.*, 1996), in agreement with expectations (Atkinson, 1994, 1997a,b), and these and other data obtained in this laboratory have been used to develop an estimation method allowing calculation of the rates of reaction of alkoxy radicals (Atkinson, 1997a,b; Aschmann and Atkinson, 1999).

In this two-year experimental program, we have investigated the atmospheric chemistry of three

model C<sub>10</sub> alkanes, chosen as representative components of mineral spirits: *n*-decane as a model linear alkane, 3,4-diethylhexane as a model branched alkane, and *n*-butylcyclohexane as a model cyclic alkane.

As an integral part of this investigation of the atmospheric chemistry of C<sub>10</sub> alkanes, we have developed methods to quantify hydroxycarbonyls and hydroxynitrates formed from the OH radical-initiated reactions of alkanes, and have re-investigated selected aspects of the atmospheric chemistry of *n*-pentane, *n*-hexane, *n*-heptane and *n*-octane.

Specifically, we addressed the following two Tasks during this contract:

Task #1. To develop methods to identify and quantify hydroxycarbonyls and hydroxynitrates formed from the OH radical-initiated reactions of alkanes (including cyclic alkanes). Once developed, these techniques were to be used for product studies of the three C<sub>10</sub> alkanes (see Task 2 below), and can obviously be used in the future to identify and quantify hydroxycarbonyls and hydroxynitrates from the NO-air photooxidations of other volatile organic compounds. We also planned to re-measured the octyl nitrate yield from the *n*-octane reaction to compare with our previous data (Atkinson *et al.*, 1982a).

Task #2. To measure room temperature rate constants for the reactions of the OH radical with 3,4-diethylhexane and *n*-butylcyclohexane (that for *n*-decane has been measured previously in this and other laboratories), and to identify and, if possible, quantify the products of the reactions of the OH radical with *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane.

To accomplish Task 1 we extended our previous study of the OH radical-initiated reaction of *n*-pentane (Atkinson *et al.*, 1995a), using sampling, analysis and calibration procedures which are significantly improved over those employed in our early 1980's studies (Atkinson *et al.*, 1982a, 1983), to re-investigate alkyl nitrate formation from the reactions of the OH radical with *n*-hexane through *n*-octane. In addition, we used API-MS/MS in the negative ion mode to investigate products of the *n*-pentane through *n*-octane and *n*-pentane-d<sub>12</sub> through *n*-octane-d<sub>18</sub> reactions, with the goal of observing the formation of the hydroxyalkyl nitrates predicted to be formed subsequent to alkoxy radical isomerization and quantifying hydroxyalkyl nitrate and hydroxycarbonyl products. The techniques developed in Task 1 were then used in Task 2 to investigate the atmospheric chemistry of *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane. For convenience, Tasks 1 and 2 are described below in separate sections.

## TASK 1: ANALYSES OF HYDROXYCARBONYLS, HYDROXYNITRATES AND ALKYL NITRATES FROM THE NO<sub>x</sub>-PHOTOOXIDATIONS OF C<sub>5</sub>-C<sub>8</sub> *n*-ALKANES

### Experimental Methods

Experiments were carried out at  $298 \pm 2$  K and 740 Torr total pressure of air in a 7900 liter 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 liter 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 (Atkinson *et al.*, 1981), and NO was added to the reactant mixtures to suppress the formation of O<sub>3</sub> and hence of NO<sub>3</sub> radicals (Atkinson *et al.*, 1981).

#### *Teflon Chamber with Analysis by GC-FID*

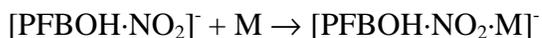
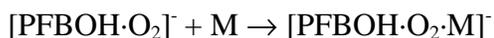
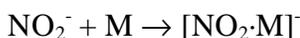
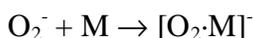
For the OH radical reactions carried out in the 7900 liter Teflon chamber (at ~5% relative humidity), the initial reactant concentrations (in molecule cm<sup>-3</sup> units) were: CH<sub>3</sub>ONO, (2.2-2.5) × 10<sup>14</sup>; NO, (2.2-2.3) × 10<sup>14</sup>; and *n*-alkane, (2.34-2.51) × 10<sup>13</sup>. 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<sup>3</sup> 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<sup>-1</sup>. 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 for the alkanes and selected products were determined by introducing measured amounts of the chemicals into the 7900 liter chamber and conducting several replicate GC-FID analyses (Atkinson *et al.*, 1995b). 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 (Scanlon and Willis, 1985), verifying that wall losses in these calibrations were minor or negligible, in contrast to what is now suspected for our previous study (Atkinson *et al.*, 1982a). The unique MS fragmentation patterns of the alkyl nitrates allowed the various isomers to be distinguished from one another. NO and initial NO<sub>2</sub> concentrations were measured using a Thermo Environmental Instruments, Inc., Model 42 NO-NO<sub>2</sub>-NO<sub>x</sub> 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 x 75 cm length Pyrex tube at  $\sim 20$  liter  $\text{min}^{-1}$  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 (Kwok *et al.*, 1996; Aschmann *et al.*, 1997). 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 (Aschmann *et al.*, 1997).

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 ( $\text{O}_2^-$ ), its hydrates [ $\text{O}_2^-(\text{H}_2\text{O})_n$ ], and  $\text{O}_2$  clusters [ $\text{O}_2^-(\text{O}_2)_n$ ] are the major reagent negative ions in the chamber diluent air (French *et al.*, 1985). Other reagent ions, for example,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ , are then formed through reactions between the primary reagent ions and neutral molecules such as  $\text{NO}_2$ , and instrument tuning and operation were designed to induce cluster formation (Kwok *et al.*, 1996; Aschmann *et al.*, 1997). 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 pin-hole in the cap of the vial).

Under the experimental conditions used, analytes were detected as adduct ions formed from reaction of the neutral analyte (M) and reagent ions such as  $\text{O}_2^-$ ,  $\text{NO}_2^-$ , [ $\text{PFBOH}\cdot\text{O}_2$ ] $^-$  and [ $\text{PFBOH}\cdot\text{NO}_2$ ] $^-$  generated in the ion source region. For example,



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  $\text{CH}_3\text{ONO}$ ,  $\text{NO}$  and *n*-alkane (or deuterated *n*-alkane) were  $\sim(2.4\text{-}24) \times 10^{12}$  molecule  $\text{cm}^{-3}$  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 2.5-5 min.

### Chemicals

The chemicals used, and their stated purities, were: *n*-heptane, Mallinckrodt; *n*-heptane- $\text{d}_{16}$  (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 Company; *n*-hexane-*d*<sub>14</sub> (99%), *n*-octane-*d*<sub>18</sub> (99%) and *n*-pentane-*d*<sub>12</sub> (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 (≥99.0% and *cis*-2-butene (≥95%), Matheson Gas Products. Methyl nitrite was prepared and stored as described previously (Atkinson *et al.*, 1981).

## Results and Discussion

### *GC-FID and GC-MS Analyses of Alkyl Nitrates*

GC-MS analyses of irradiated CH<sub>3</sub>ONO - 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 alkane reactants and 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 (Atkinson *et al.*, 1982a) using rate constants for reactions of the OH radical (in units of 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) of: *n*-hexane, 5.45; *n*-heptane, 7.01; *n*-octane, 8.71; 2-hexyl nitrate, 3.06; 3-hexyl nitrate, 2.60; 2-heptyl 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 (1997a), those for 2- and 3-hexyl nitrate were those cited in Atkinson (1989) and re-evaluated using the recently recommended rate constant for the reference organic cyclohexane (Atkinson, 1997a), and those for the heptyl and octyl nitrates were calculated (Atkinson, 2000b) using the group rate constants and group substituent factors given by Atkinson (2000b) and decreased by 3.6% to account for the recent reference organic recommendations of Atkinson (1997a). 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 + alkyl nitrate)/k(OH + *n*-alkane) and with the extent of reaction (Atkinson *et al.*, 1982a), 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 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 (Atkinson *et al.*, 1995a) 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<sub>2</sub> [reaction (7)].



The rate constant for reaction (7) is ~3.8 x 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> at room temperature (Atkinson, 1997a). The final NO concentrations in the experiments were >1.0 x 10<sup>14</sup> molecule cm<sup>-3</sup>, and with the expectation that ([NO] + [NO<sub>2</sub>]) ~ constant throughout the irradiations (Atkinson *et al.*, 1989) then the maximum NO<sub>2</sub>

concentrations were  $<1.3 \times 10^{14}$  molecule  $\text{cm}^{-3}$ , corresponding to a reaction rate of alkoxy radicals due to reaction with  $\text{NO}_2$  of  $<5 \times 10^3 \text{ s}^{-1}$ . All of the alkoxy radicals formed from *n*-hexane, *n*-heptane and *n*-octane can isomerize through a 6-membered transition state (Atkinson, 1997a,b), with estimated isomerization rate constants at 298 K of  $\sim 2 \times 10^5 \text{ s}^{-1}$  for the 3-hexoxy radical,  $\sim 4 \times 10^5 \text{ s}^{-1}$  for the 4-heptoxy radical, and  $\geq 2 \times 10^6 \text{ s}^{-1}$  for the 2-hexoxy, 2- and 3-heptoxy and 2-, 3- and 4-octoxy radicals (Atkinson, 1997a,b). 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, respectively (per 3-hexoxy or 4-heptoxy radical formed) 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.

Our present alkyl nitrate yields, together with the pentyl nitrate yields from *n*-pentane (Atkinson *et al.*, 1995a), are compared to our previous early 1980's data (Atkinson *et al.*, 1982a) in Table 1, showing that while our more recent pentyl nitrates yield (Atkinson *et al.*, 1995a) is in agreement with the earlier data of Atkinson *et al.* (1982a), our present alkyl nitrate yields from *n*-hexane, *n*-heptane and *n*-octane are significantly lower than our previous data (Atkinson *et al.*, 1982a). The previous measurements (Atkinson *et al.*, 1982a) were carried out in an  $\sim 60$  liter Teflon reaction vessel with GC-FID analyses on a packed column, with  $100 \text{ cm}^3$  samples being collected in a gas-tight 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 liter volume borosilicate glass vessel with replicate sampling and analysis. We now believe that this earlier study (Atkinson *et al.*, 1982a) had the potential for losses of the larger ( $\geq \text{C}_6$ ) alkyl nitrates during the experiments, including (especially) during the alkyl nitrate calibrations, and that the data obtained may have been subject to significant (and then unrecognized) uncertainties. Our present total heptyl nitrates yield of  $0.178 \pm 0.024$  at  $298 \pm 2 \text{ K}$  and 740 Torr total pressure of air is in good agreement with the total yield of heptyl nitrates measured by Harris and Kerr (1989) at 730 Torr total pressure of air of  $0.201 \pm 0.041$  at 298 K and  $0.180 \pm 0.015$  at 299 K, although the heptyl nitrate isomer distribution reported by Harris and Kerr (1989) differed significantly from our present and previous (Atkinson *et al.*, 1982a, 1983) heptyl nitrate isomer distributions. It should be noted that Harris and Kerr (1989) 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.

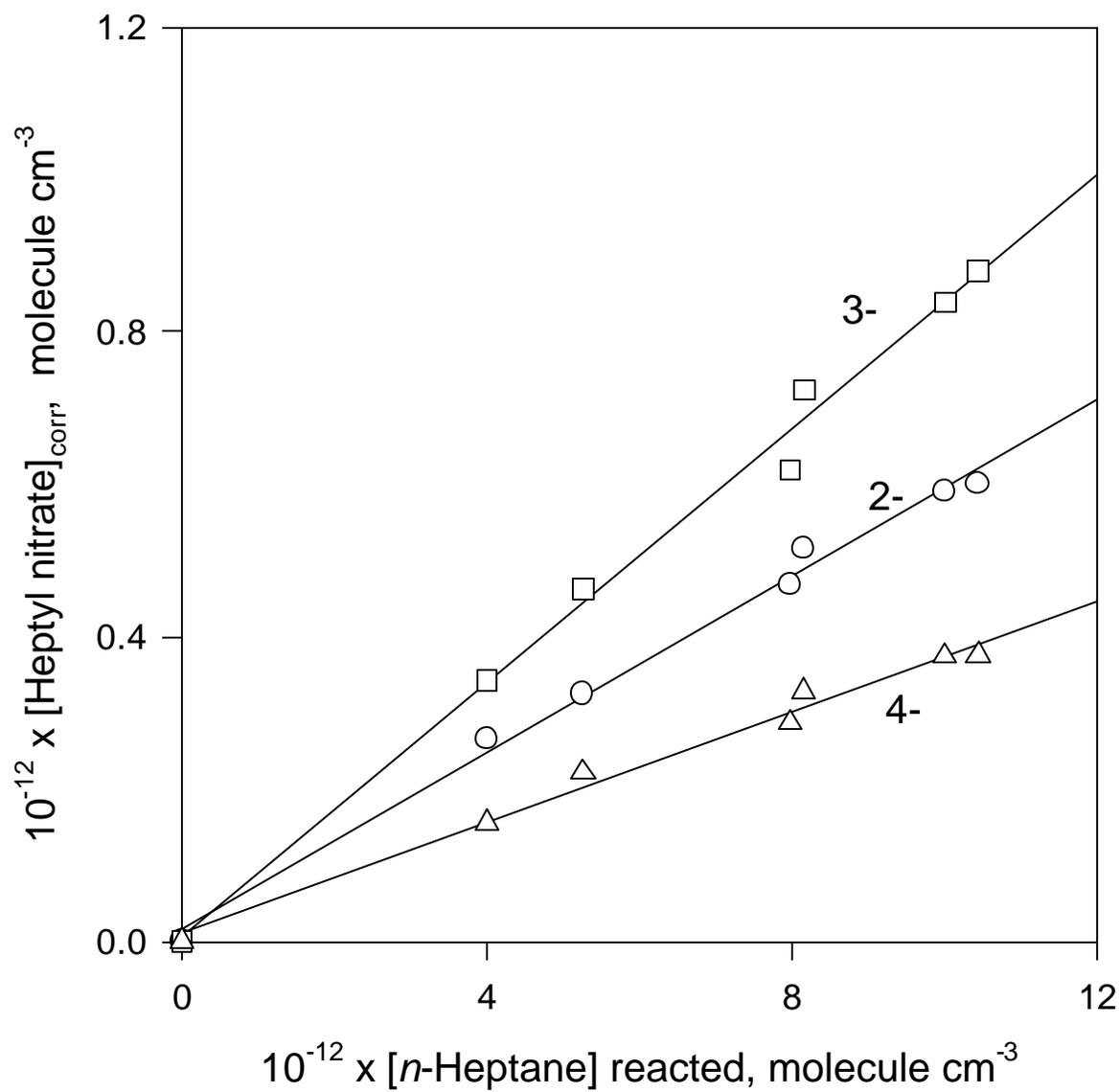


Figure 1. Plots of the amounts of 2-, 3- and 4-heptyl nitrate formed, corrected for reaction with the OH radical (see text), against the amounts of *n*-heptane reacted with the OH radical in the presence of NO.

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  $298 \pm 2$  K and atmospheric pressure of air.<sup>a</sup>

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

<sup>a</sup>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  $\pm 5\%$  each.

<sup>b</sup>From least-squares analyses of the sum of the nitrates.

<sup>c</sup>From Atkinson *et al.* (1982a), with the indicated errors being two least-squares standard deviations.

<sup>d</sup>From Atkinson *et al.* (1995a); 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  $298 \pm 2$  K and atmospheric pressure of air.

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

<sup>a</sup>Using the -CH<sub>3</sub> and -CH<sub>2</sub>- group rate constants and group substituent factors of method of Kwok and Atkinson (1995) to calculate the fractions of the overall OH radical reaction proceeding by C-H abstraction at the individual carbon atoms.

<sup>b</sup>From least-squares analyses of the sum of the nitrates, using the method of Kwok and Atkinson (1995) to calculate the fraction of the overall OH radical reaction proceeding by C-H abstraction from secondary -CH<sub>2</sub>- groups.

<sup>c</sup>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.

<sup>d</sup>From Atkinson *et al.* (1995a); see text.

Table 1 also contains the alkyl nitrate formation yields reported by Atkinson *et al.* (1982a) 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  $0.0354 \pm 0.0026$  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 (Atkinson *et al.*, 1982a, 1983). In the absence of direct experimental data, the estimation method of Kwok and Atkinson (1995) 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<sub>3</sub> and -CH<sub>2</sub>- groups in the *n*-alkanes, and hence the fractions of the overall OH radical reaction proceeding at the various -CH<sub>2</sub>- groups. Table 2 gives the formation yields of the 2-, 3- and 4-alkyl nitrates from their precursor secondary RO<sub>2</sub><sup>•</sup> radicals [*i.e.*, rate constant ratios  $k_{3a}/(k_{3a} + k_{3b})$ ] derived from our present and previous (Atkinson *et al.*, 1982a, 1995a) data and the calculated fractions of the overall OH radical reaction proceeding at the 2-, 3- and 4-position -CH<sub>2</sub>- groups (Kwok and Atkinson, 1995). It needs to be recognized that while the calculated overall rate constants for the reaction of the OH radical with the C<sub>2</sub>-C<sub>8</sub> *n*-alkanes at 298 K agree with the recommended values (Atkinson, 1997a) to within 13%, the calculated partial rate constants and hence fractions of the overall reaction proceeding at the various -CH<sub>3</sub> and -CH<sub>2</sub>- groups may be less reliable (Atkinson *et al.*, 1995a).

The secondary alkyl nitrate formation yields from the corresponding RO<sub>2</sub><sup>•</sup> radicals given in Table 2 show that the nitrate yield increases with the carbon number, as observed previously (Atkinson *et al.*, 1982a). Table 2 also shows that the nitrate yields from the various secondary RO<sub>2</sub><sup>•</sup> 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  $1.35 \pm 0.15$  (two standard deviations), and this ratio can be compared with that of 1.23 obtained from the estimation method of Kwok and Atkinson (1995) assuming that for a given *n*-alkane the secondary alkyl nitrate yield per RO<sub>2</sub><sup>•</sup> precursor radical is identical. Given the likely uncertainties in the substituent group factors in the estimation method (Atkinson, 1987; Kwok and Atkinson, 1995), our data are consistent with the secondary alkyl nitrate yield per RO<sub>2</sub><sup>•</sup> 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.* (1982a, 1995a) and this work] and cyclohexane [data from Aschmann *et al.* (1997)] against carbon number is shown in Figure 2. The cyclohexyl nitrate yield of Aschmann *et al.* (1997) of  $0.165 \pm 0.021$  at  $298 \pm 2$  K and 740 Torr pressure of air is in good agreement with the yields reported by Platz *et al.* (1999) [ $0.16 \pm 0.04$  at  $296 \pm 2$  K and 700 Torr total pressure] and Orlando *et al.* (2000) [ $0.15 \pm 0.04$  at 296 K and 700 Torr

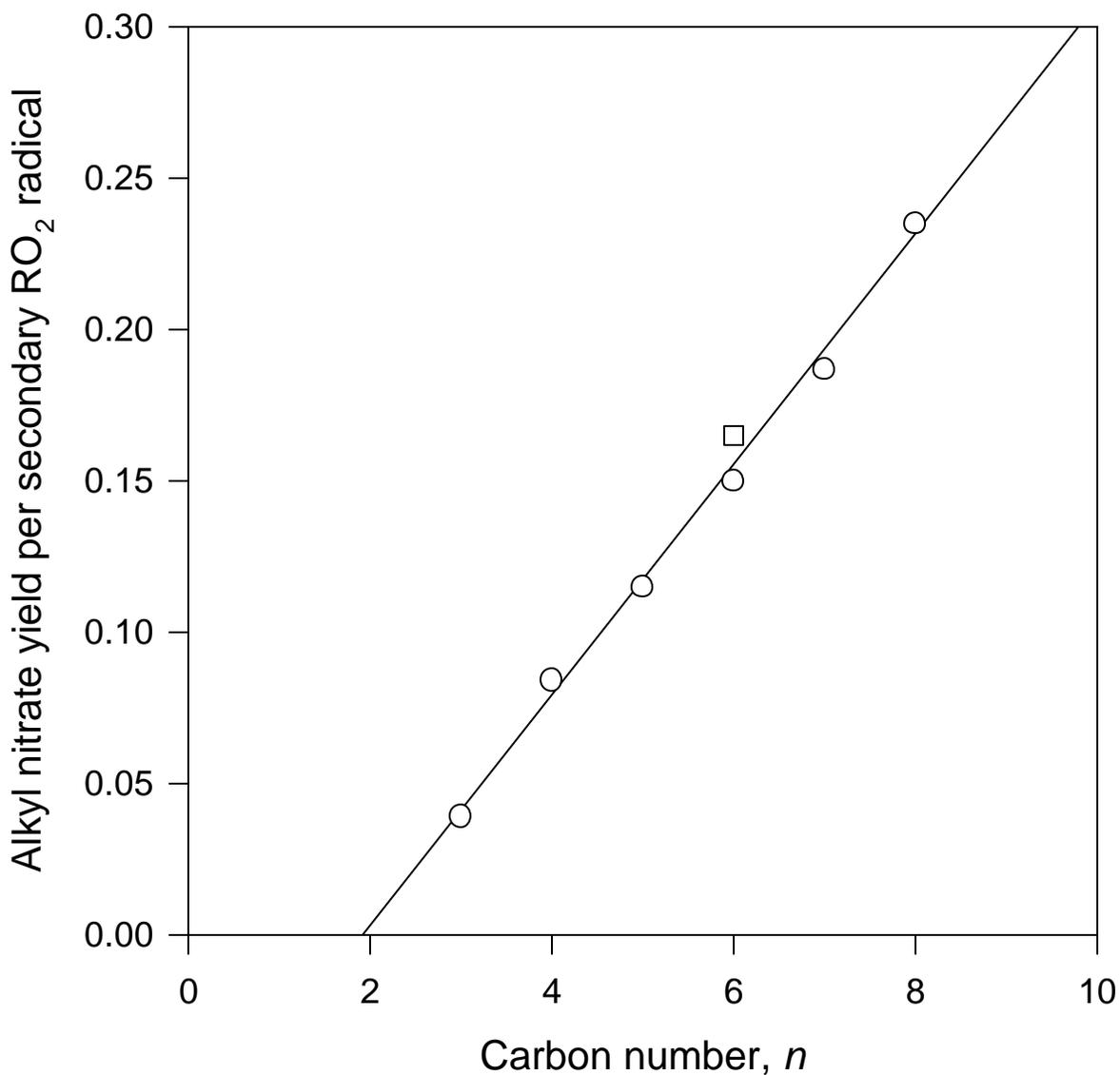


Figure 2. Plot of the yields of secondary alkyl nitrates from their precursor secondary alkyl peroxy radicals,  $k_{3a}/(k_{3a} + k_{3b})$ , for the C<sub>3</sub>-C<sub>8</sub> *n*-alkanes (O) and cyclohexane (□) against carbon number of the alkane. The data for the propane and *n*-butane reactions are from Atkinson *et al.* (1982a); for the *n*-pentane reaction are from Atkinson *et al.* (1995a); and for the cyclohexane reaction are from Aschmann *et al.* (1997).

total pressure], but is higher than the value of  $0.090 \pm 0.044$  at atmospheric pressure and room temperature measured by Takagi *et al.* (1981). The nitrate yield per secondary  $\text{RO}_2^\bullet$  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  $\text{RO}_2^\bullet$  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  $>\text{C}_8$  alkanes (Carter and Atkinson, 1989). Our present data can be used with previous literature data for alkyl nitrate formation from propane (Atkinson *et al.*, 1982a), *n*-butane (Atkinson *et al.*, 1982a), *n*-pentane (Atkinson *et al.*, 1995a), 2-methylbutane (Atkinson *et al.*, 1984, 1987), 2-methylpentane (Atkinson *et al.*, 1984), 3-methylpentane (Atkinson *et al.*, 1984, 1987), cyclohexane (Aschmann *et al.*, 1997; Platz *et al.*, 1999; Orlando *et al.*, 2000), and *n*-heptane (Harris and Kerr, 1989) to revise the formula proposed by Carter and Atkinson (1989).

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

where

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

and

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

in which  $Y_0^{298}[\text{M}]$  and  $Y_\infty^{298}$  are the limiting low-pressure and high-pressure rate constant ratios  $k_{3a}/k_{3b}$  at 298 K, respectively,  $[\text{M}]$  is the concentration of diluent air,  $F$ ,  $m_o$ ,  $m_\infty$ ,  $\alpha$  and  $\beta$  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.* (1983) 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 Equation (I):  $\alpha = 2 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1}$ ,  $\beta = 1.0$ ,  $Y_\infty^{298} = 0.43$ ,  $F = 0.41$ ,  $m_o = 0$ , and  $m_\infty = 8.0$ . The major difference between these revised parameters and those given in Carter and Atkinson (1989) is in the value of  $Y_\infty^{298}$ , with Carter and Atkinson (1989) 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 (Carter and Atkinson, 1989) prediction for  $n > 5$ .

### API-MS Analyses

A series of  $\text{CH}_3\text{ONO} - \text{NO} - n\text{-alkane} - \text{air}$  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  $\text{NO}_2$  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 (Aschmann *et al.*, 1997, 1998; Tuazon *et al.*, 1999). PFBOH has a strong response in the negative ion mode and readily forms dimers as well as adduct ions with  $\text{O}_2^-$  and  $\text{NO}_2^-$  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- $\text{d}_{12}$  through  $n$ -octane- $\text{d}_{18}$ . 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  $\text{CH}_3\text{ONO} - \text{NO} - n\text{-hexane} - \text{air}$  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 -  $\text{CH}_3\text{ONO} - \text{NO} - \text{air}$  mixture prior to irradiation) can be attributed to dimers of PFBOH forming adducts with  $\text{O}_2$ ,  $\text{NO}_2$ , NO and  $\text{H}_2\text{O}$ . The NO and  $\text{NO}_2$  adducts are present from the  $\text{CH}_3\text{ONO} - \text{NO} - \text{air}$  mixture used to generate OH radicals and the NO concentration decreases, and the  $\text{NO}_2$  concentration increases, as the reaction proceeds. As shown in Figure 4, an API-MS/MS "precursor ion" scan of 230 u (which corresponds to  $[\text{PFBOH}\cdot\text{O}_2]^-$ ) 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 Figures 5A and 5B, respectively. In general, API-MS/MS "product ion" spectra of the adduct ions  $[\text{PFBOH}\cdot\text{O}_2\cdot\text{M}]^-$  show a prominent fragment ion at 230 u  $[\text{PFBOH}\cdot\text{O}_2]^-$ , 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)

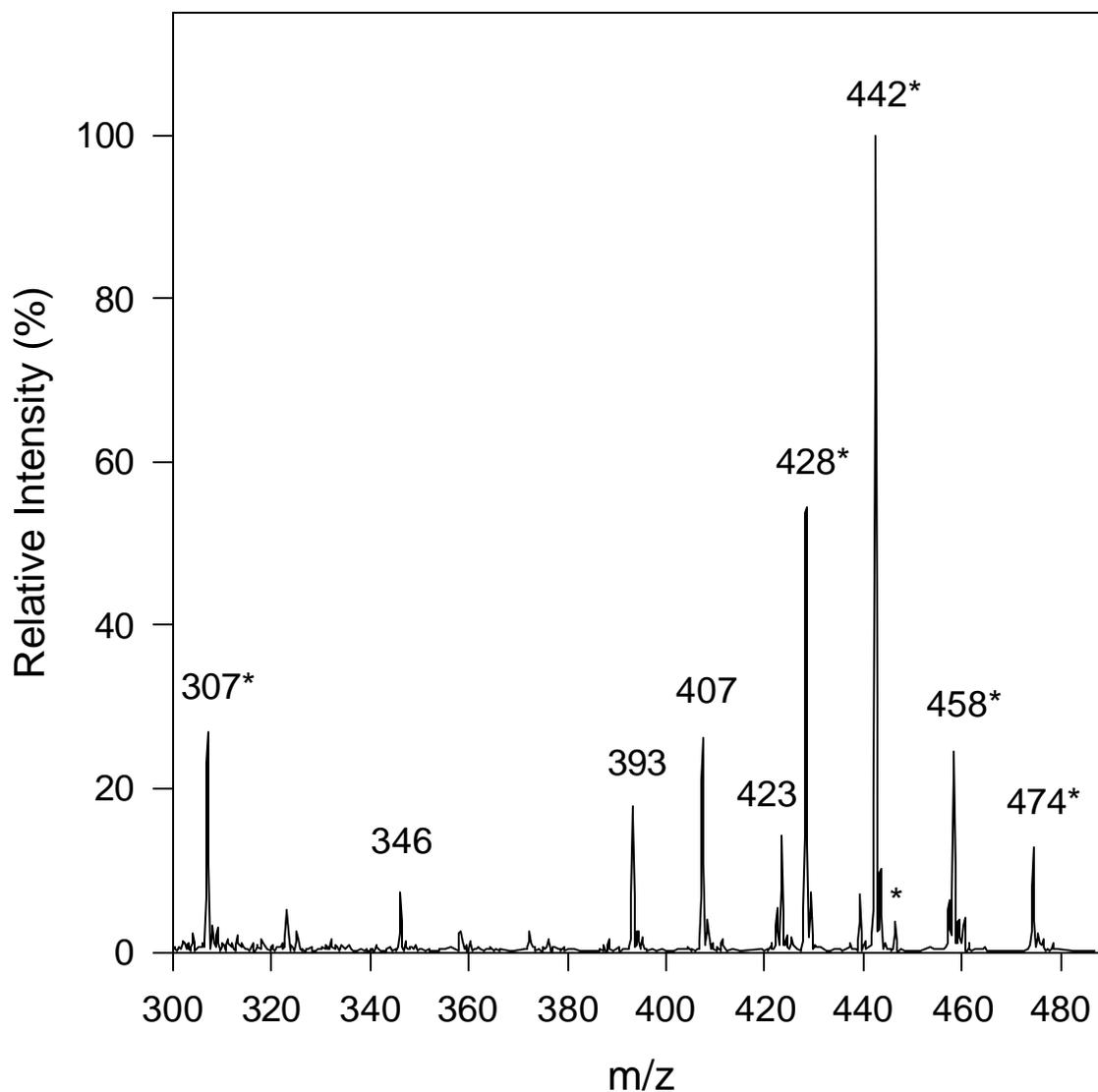


Figure 3. API-MS negative ion spectrum (300-500 u) of an irradiated  $\text{CH}_3\text{ONO} - \text{NO} - n$ -hexane - air mixture, with addition of pentafluorobenzyl alcohol (PFBOH) to the sampled air stream. The ion peaks marked with (\*) are attributed to: 428 u,  $[(\text{PFBOH})_2\text{O}_2]^-$ ; 442 u,  $[(\text{PFBOH})_2\text{NO}_2]^-$ ; 446 u,  $[(\text{PFBOH})_2\text{O}_2\text{H}_2\text{O}]^-$ ; 458 u,  $[(\text{PFBOH})_2\text{O}_2\text{NO}]^-$ ; and 474 u,  $[(\text{PFBOH})_2\text{O}_2\text{NO}_2]^-$ . The 307 u ion peak is always present when the PFBOH is added and may be due to a proton transfer reaction.

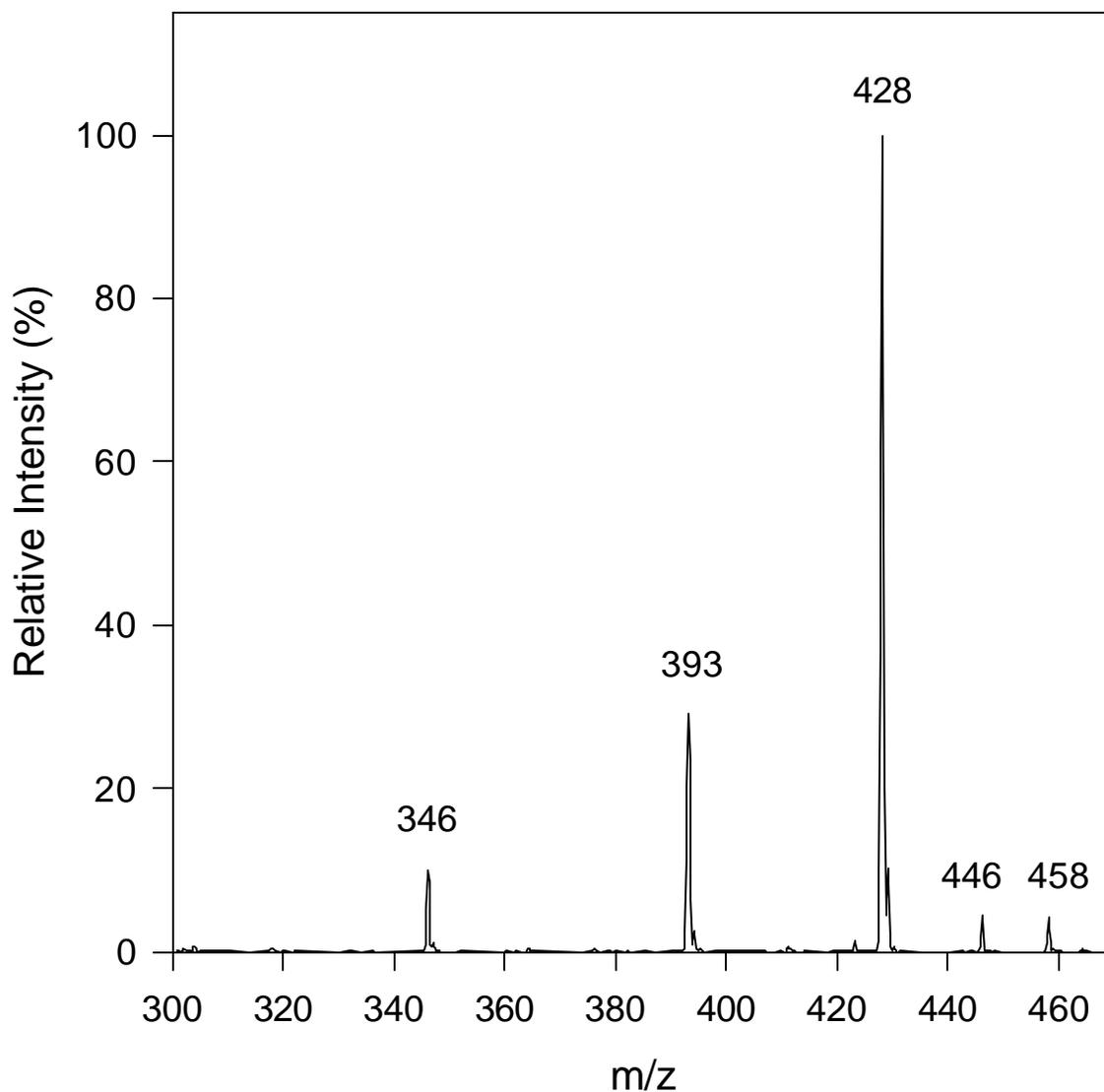


Figure 4. API-MS/MS CAD "precursor ion" negative ion spectrum of the 230 u  $[\text{PFBOH}\cdot\text{O}_2]^-$  ion for the same experiment as in Figure 3. The ion peaks at 428, 446 and 458 u are attributed as noted in Figure 3. The 346 and 393 u ion peaks indicate two products of the *n*-hexane reaction.

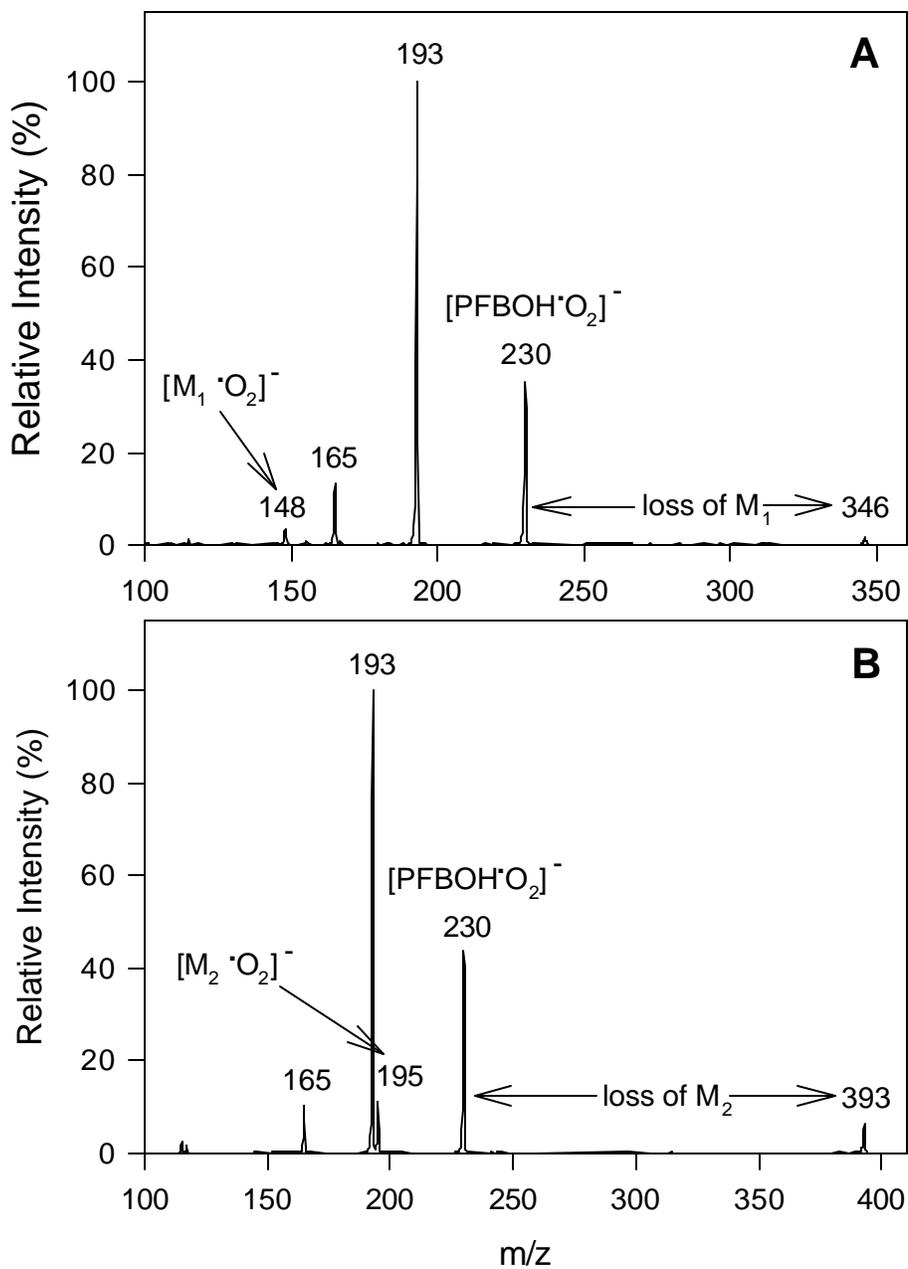


Figure 5. API-MS/MS CAD "product ion" negative ion spectra of the ion peaks at 346 u and 393 u observed in the API-MS/MS CAD "precursor ion" spectrum of the 230 u [PFBOH·O<sub>2</sub>]<sup>-</sup> ion shown in Figure 4. (A) The molecular weight 116 product (M<sub>1</sub>) is seen from the loss of M<sub>1</sub> from the parent adduct ion [PFBOH·O<sub>2</sub>·M<sub>1</sub>]<sup>-</sup> - [M<sub>1</sub>] = 230 u and by the presence of a fragment ion that is the O<sub>2</sub><sup>-</sup> adduct at 148 u. (B) The molecular weight 163 product (M<sub>2</sub>) is seen from the loss of M<sub>2</sub> from the parent adduct ion [PFBOH·O<sub>2</sub>·M<sub>2</sub>]<sup>-</sup> - [M<sub>2</sub>] = 230 u and by the presence of a fragment ion that is the O<sub>2</sub><sup>-</sup> adduct at 195 u. The 230, 193 and 165 u ion fragments are characteristic of PFBOH.

are indicated from the API-MS/MS spectra in Figures 5A and 5B, respectively. These products are also evident from the less abundant fragment ions at 148 u and 195 u, corresponding to  $[M-O_2]^-$  formed from loss of PFBOH from the parent ion, that are also seen in Figure 5A and 5B, 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 (Kwok *et al.*, 1995, 1996; Atkinson *et al.*, 1995a; Aschmann *et al.*, 1997), 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 analogs) are attributed to the 1,4-hydroxynitrates formed as shown in Scheme 1. The  $C_nH_{2n-1}(O)(OH)$  species (and their deuterated analogs) are attributed to the 1,4-hydroxycarbonyls formed as also shown in Scheme 1 and previously observed by us (Atkinson *et al.*, 1995a; Kwok *et al.*, 1996; Aschmann *et al.*, 1997) 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.* (1995) using GC-MS analyses after derivatization by 2,4-dinitrophenylhydrazine.

Table 3. Product species observed from the reactions of the OH radical with *n*-alkanes in the presence of NO, from the presence of  $[PFBOH \cdot O_2 \cdot M]^-$  adduct ions.

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

While the formation of [PFBOH·O<sub>2</sub>·M]<sup>-</sup> 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<sub>2</sub><sup>-</sup> ions with PFBOH (to form [PFBOH·NO<sub>2</sub>]<sup>-</sup> adducts) competed with the corresponding reaction of O<sub>2</sub><sup>-</sup> ions with PFBOH at NO<sub>2</sub> concentrations of ≥10<sup>12</sup> molecule cm<sup>-3</sup>. For example, in Figure 3 the ion peak at 407 u is attributed to the [PFBOH·NO<sub>2</sub>]<sup>-</sup> adduct with the hydroxynitrate. However, the corresponding adduct did not form with the hydroxycarbonyl and as the NO<sub>2</sub> increased during the reaction, the signal for the [PFBOH·O<sub>2</sub>·hydroxycarbonyl]<sup>-</sup> adduct at 346 u disappeared. Therefore, because NO<sub>2</sub> is formed from the photooxidation of methyl nitrite (and also from reactions of HO<sub>2</sub> and organic peroxy radicals with NO), this limited the potential of using [PFBOH·O<sub>2</sub>·M]<sup>-</sup> ions for quantification.

*NO<sub>2</sub> Addition.* It was observed that in the absence of PFBOH, the hydroxycarbonyls and hydroxyalkyl nitrates formed adducts with O<sub>2</sub><sup>-</sup> and with NO<sub>2</sub><sup>-</sup> ions and that the majority of the adducts at the end of the alkane photooxidation were NO<sub>2</sub><sup>-</sup> adducts. Figure 6 shows an API-MS spectrum of an irradiated CH<sub>3</sub>ONO - NO - *n*-pentane - *n*-hexane - *n*-heptane - *n*-octane - air mixture, with the C<sub>5</sub>- through C<sub>8</sub>-hydroxycarbonyls observed as their NO<sub>2</sub><sup>-</sup> adducts at 148, 162, 176 and 190 u, respectively, and the C<sub>5</sub>- through C<sub>8</sub>-hydroxyalkyl nitrates observed as their NO<sub>2</sub><sup>-</sup> adducts at 195, 209, 223 and 237 u, respectively.

API-MS/MS "precursor ion" spectra of the 32 u O<sub>2</sub><sup>-</sup> ion and the 46 u NO<sub>2</sub><sup>-</sup> ion showed that reactions of the NO<sub>2</sub><sup>-</sup> ion to form the [NO<sub>2</sub>·M]<sup>-</sup> adducts dominated over the corresponding reactions of the O<sub>2</sub><sup>-</sup> ion at NO<sub>2</sub> concentrations ≥(2-3) × 10<sup>13</sup> molecule cm<sup>-3</sup>, and that with these NO<sub>2</sub> concentrations the dominant ion peaks involving the hydroxycarbonyls and hydroxyalkyl nitrates were the [NO<sub>2</sub>·M]<sup>-</sup> ions.

Therefore addition of NO<sub>2</sub> after the reaction was employed to quantify the hydroxy-carbonyl and hydroxyalkyl nitrates in these OH radical-initiated reactions, with an internal standard of similar chemical structure as the reaction products 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) × 10<sup>13</sup> molecule cm<sup>-3</sup> of NO<sub>2</sub> (the concentrations of the hydroxycarbonyls in the chamber were in the range (2.4-24) × 10<sup>11</sup> molecule cm<sup>-3</sup>). The API-MS spectra obtained from two independent experiments showed that the intensities of the [NO<sub>2</sub>·hydroxycarbonyl]<sup>-</sup> adducts depended on the particular hydroxycarbonyl M, with the relative API-MS ion intensities of the [NO<sub>2</sub>·hydroxycarbonyl]<sup>-</sup> adducts for equal concentrations of the hydroxycarbonyls being: 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 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<sub>3</sub>CH(ONO<sub>2</sub>)CH(OH)CH<sub>3</sub> was formed *in situ* in the chamber from reaction of the OH radical with *cis*-2-butene and used as the internal standard for quantification of the 1,4-hydroxyalkyl nitrates, (assuming an average of the literature formation yields measured by Muthuramu *et al.* (1993) [0.037±0.009] and O'Brien *et al.* (1998) [0.034± 0.005]).

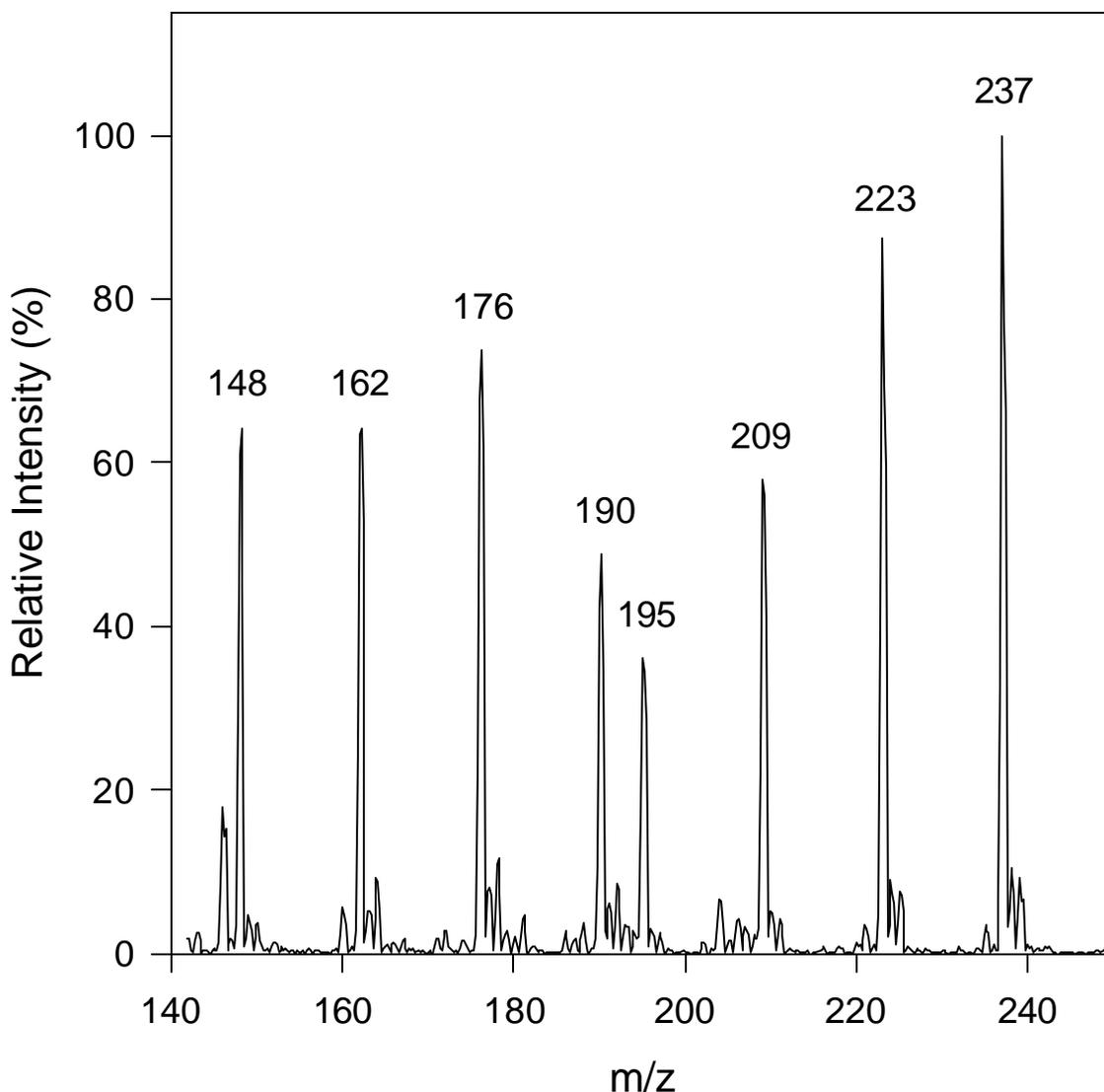


Figure 6. API-MS negative ion spectrum of an irradiated  $\text{CH}_3\text{ONO} - \text{NO} - n\text{-pentane} - n\text{-hexane} - n\text{-heptane} - n\text{-octane} - \text{air}$  mixture, with  $\text{NO}_2$  added to the chamber after the irradiation and an  $\text{NO}_2$  concentration of  $3 \times 10^{13}$  molecule  $\text{cm}^{-3}$ . The initial  $n$ -alkane concentrations were each  $\sim 2.2 \times 10^{12}$  molecule  $\text{cm}^{-3}$  and the extents of reaction ranged from 5.6% for  $n$ -pentane to 13% for  $n$ -octane. The  $\text{C}_5$ - through  $\text{C}_8$ -hydroxycarbonyls are observed as their  $\text{NO}_2^-$  adducts at 148, 162, 176 and 190 u, respectively, and the  $\text{C}_5$ - through  $\text{C}_8$ -hydroxyalkyl nitrates are observed as their  $\text{NO}_2^-$  adducts at 195, 209, 223 and 237 u, respectively. The concentration of the  $\text{C}_5$ -hydroxyalkyl nitrate (expected to be almost totally 4-nitrooxypentan-1-ol) is estimated to be  $3.3 \times 10^9$  molecule  $\text{cm}^{-3}$ .

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<sub>n</sub>-hydroxycarbonyl from the C<sub>n</sub> *n*-alkane, these experiments showed the formation (numbers in parentheses are the percents relative to the C<sub>n</sub>-hydroxycarbonyl) of C<sub>4</sub>- (25%), C<sub>5</sub>- (15%), C<sub>6</sub>- (11%) and C<sub>7</sub>-hydroxycarbonyls (21%) from the *n*-octane reaction, C<sub>4</sub>- (14%), C<sub>5</sub>- (10%) and C<sub>6</sub>-hydroxycarbonyls (12%) from the *n*-heptane reaction, and C<sub>4</sub>- (10%) and C<sub>5</sub>-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<sub>2</sub><sup>-</sup> adducts of C<sub>n-1</sub> hydroxycarbonyls were in part O<sub>2</sub><sup>-</sup> adducts of the C<sub>n</sub> 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) × 10<sup>13</sup> molecule cm<sup>-3</sup>, 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<sub>3</sub>ONO - 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<sub>n</sub>-hydroxyalkyl nitrate) of C<sub>5</sub>- (3%), C<sub>6</sub>- (3%) and C<sub>7</sub>-hydroxyalkyl nitrates (7%) from the *n*-octane reaction, C<sub>5</sub>- (1.5%) and C<sub>6</sub>-hydroxyalkyl nitrates (6.5%) from the *n*-heptane reaction, and C<sub>5</sub>-hydroxyalkyl nitrates (9%) from the *n*-hexane reaction.

In two of the experiments with all four *n*-alkanes present, CH<sub>3</sub>CH(OH)CH(ONO<sub>2</sub>)CH<sub>3</sub> 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 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 × 10<sup>9</sup> molecule cm<sup>-3</sup>); indeed, dilution of the chamber contents by a factor of 8 indicated that 10 ppt mixing ratios (2 × 10<sup>8</sup> molecule cm<sup>-3</sup>) of these hydroxyalkyl nitrates could still be readily observed.

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.* (1995) for the formation of 5-nitrooxyhexan-2-ol of 0.03-0.04.

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<sub>2</sub><sup>-</sup> as the reagent ion.

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

<sup>a</sup>From five experiments with all four *n*-alkanes in each irradiated CH<sub>3</sub>ONO - NO - *n*-alkane - air mixture. Indicated errors are one standard deviation.

<sup>b</sup>Yield for each alkane from an irradiated CH<sub>3</sub>ONO - 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.

<sup>c</sup>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.

<sup>d</sup>From two of the above five experiments with CH<sub>3</sub>CH(OH)CH(ONO<sub>2</sub>)CH<sub>3</sub> 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.

## TASK 2: ATMOSPHERIC CHEMISTRY OF *n*-DECANE, 3,4-DIETHYLHEXANE AND *n*-BUTYLCYCLOHEXANE

### Experimental Methods

Experiments were carried out at  $298 \pm 2$  K and 740 Torr total pressure of air in a ~8000 liter Teflon chamber with analysis by GC-FID and GC-MS, with irradiation provided by two parallel banks of blacklamps; and in a 7300 liter 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 (Atkinson *et al.*, 1981), and NO was added to the reactant mixtures to suppress the formation of O<sub>3</sub> and hence of NO<sub>3</sub> radicals.

#### *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, whose OH radical reaction rate constant is reliably known, were measured in the presence of OH radicals (Atkinson *et al.*, 1981). Providing that the alkanes and the reference compound reacted only with OH radicals, then

$$\ln \left( \frac{[\text{alkane}]_{t_0}}{[\text{alkane}]_t} \right) = \frac{k_{1a}}{k_{1b}} \ln \left( \frac{[\text{reference compound}]_{t_0}}{[\text{reference compound}]_t} \right) \quad (\text{II})$$

where  $[\text{alkane}]_{t_0}$  and  $[\text{reference compound}]_{t_0}$  are the concentrations of the alkane and reference compound, respectively, at time  $t_0$ ,  $[\text{alkane}]_t$  and  $[\text{reference compound}]_t$  are the corresponding concentrations at time  $t$ , and  $k_{1a}$  and  $k_{1b}$  are the rate constants for reactions (1a) and (1b), respectively.



Hence plots of  $\ln([\text{alkane}]_{t_0}/[\text{alkane}]_t)$  against  $\ln([\text{reference compound}]_{t_0}/[\text{reference compound}]_t)$  should be straight lines with slope  $k_{1a}/k_{1b}$  and zero intercept.

*n*-Octane was chosen as the reference compound, and the initial reactant concentrations (in molecule cm<sup>-3</sup> units) were: CH<sub>3</sub>ONO, 2.2 x 10<sup>14</sup>; NO, (2.2-2.3) x 10<sup>14</sup>; and alkane and *n*-octane, ~2.4 x 10<sup>13</sup> 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<sup>3</sup> 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<sup>-1</sup>. NO and initial NO<sub>2</sub> concentrations were measured using a Thermo Environmental Instruments, Inc., Model 42 chemiluminescent NO-NO<sub>x</sub> 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.

*Analysis by GC-FID and GC-MS.* For the OH radical reactions carried out in the ~8000 liter Teflon chamber (at ~5% relative humidity), the initial reactant concentrations (in molecule cm<sup>-3</sup> units) were: CH<sub>3</sub>ONO, (2.2-2.3) x 10<sup>14</sup>; NO, (2.0-2.3) x 10<sup>14</sup>; and alkane, (2.25-2.51) x 10<sup>13</sup>. 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 liter chamber and conducting several replicate GC-FID analyses (Atkinson *et al.*, 1995b). Because of a lack of commercially available standards of the various C<sub>10</sub> alkyl nitrates expected to be formed from the OH radical-initiated reactions of *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane, the molar GC-FID responses of the C<sub>10</sub> alkyl nitrates were calculated using their Equivalent Carbon Numbers [ECNs] (Scanlon and Willis, 1985), which, of course, were identical for these isomeric C<sub>10</sub> alkyl nitrates.

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. The unique MS fragmentation patterns of the *n*-alkyl nitrates allowed the various isomers formed from *n*-decane to be distinguished from one another.

NO and initial NO<sub>2</sub> concentrations were measured using a Thermo Environmental Instruments, Inc., Model 42 NO-NO<sub>2</sub>-NO<sub>x</sub> chemiluminescence analyzer.

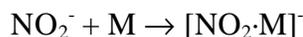
*Teflon Chamber with Analysis by API-MS.* In the experiments with API-MS analyses, the chamber contents were sampled through a 25 mm diameter x 75 cm length Pyrex tube at  $\sim 20$  liter  $\text{min}^{-1}$  directly into the API mass spectrometer source. The operation of the API-MS in the MS (scanning) and MS/MS [with collision activated dissociation (CAD)] modes has been described elsewhere (Kwok *et al.*, 1996; Aschmann *et al.*, 1997). 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 (Aschmann *et al.*, 1997).

Both positive and negative ion modes were used in these experiments. In the positive ion mode, protonated water hydrates,  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ , 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 (Kwok *et al.*, 1996; Aschmann *et al.*, 1997). 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 ( $[\text{M}+\text{H}]^+$ ) and their protonated homo- and heterodimers (Kwok *et al.*, 1996; Aschmann *et al.*, 1997).

In the negative ion mode, negative ions were generated by the negative corona around the discharge needle. The superoxide ion ( $\text{O}_2^-$ ), its hydrates  $[\text{O}_2^-(\text{H}_2\text{O})_n]$ , and  $\text{O}_2$  clusters  $[\text{O}_2^-(\text{O}_2)_n]$  are the major reagent negative ions in the chamber diluent air. Other reagent ions, for example,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ , are then formed through reactions between the primary reagent ions and neutral molecules such as  $\text{NO}_2$ , and instrument tuning and operation were designed to induce cluster formation. Under the experimental conditions used, analytes were detected as adducts ions formed from reaction of the neutral analyte (M) and the reagent ion  $\text{NO}_2^-$  (see Task 1 above and Arey *et al.*, 2001); for example,



Again, ions are drawn by an electric potential from the ion source through the sampling orifice into the mass-analyzing first quadrupole or third quadrupole, and neutral molecules and particles are prevented from entering the orifice by a flow of high-purity nitrogen ("curtain" gas).

The initial concentrations of  $\text{CH}_3\text{ONO}$ ,  $\text{NO}$  and alkane were equal and generally at  $\sim 4.8 \times 10^{12}$  molecule  $\text{cm}^{-3}$  each (in two *n*-decane experiments the initial concentrations were  $\sim 1.2 \times 10^{13}$  and  $\sim 2.4 \times 10^{13}$  molecule  $\text{cm}^{-3}$  each), and 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+%), Aldrich Chemical Company; *n*-butylcyclohexane (99%) and 3,3-diethylhexane (99%), ChemSampCo; 2-pentyl nitrate (containing 3-pentyl nitrate), Fluorochem; and NO ( $\geq 99.0\%$  and *cis*-2-butene ( $\geq 95\%$ ), Matheson Gas Products. Methyl nitrite was prepared and stored as described previously (Atkinson *et al.*, 1981).

## Results and Discussion

### *OH Radical Reaction Rate Constants*

The data obtained from irradiations of CH<sub>3</sub>ONO - NO - alkane - *n*-octane - air mixtures are plotted in accordance with Equation (II) in Figure 7, and least-squares analyses of these data result in the rate constant ratios  $k_{1a}/k_{1b}$  given in Table 5. 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  $8.67 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (Atkinson, 1997a), and the resulting rate constants  $k_{1a}$  are also listed in Table 5. 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.* (1982b), Nolting *et al.* (1988) and Behnke *et al.* (1988) also using relative rate methods. As shown in Table 5, rate constants calculated using a structure-reactivity estimation method (Kwok and Atkinson, 1995; Atkinson, 2000b) 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. 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).

Combining our room temperature rate constants with a 24-hr average OH radical concentration of  $1.0 \times 10^6 \text{ molecule cm}^{-3}$  (the global tropospheric average) (Prinn *et al.*, 1095; Hein *et al.*, 1997) leads to tropospheric lifetimes for these alkanes of 0.9 days, 1.6 days and 0.7 days for *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane, respectively.

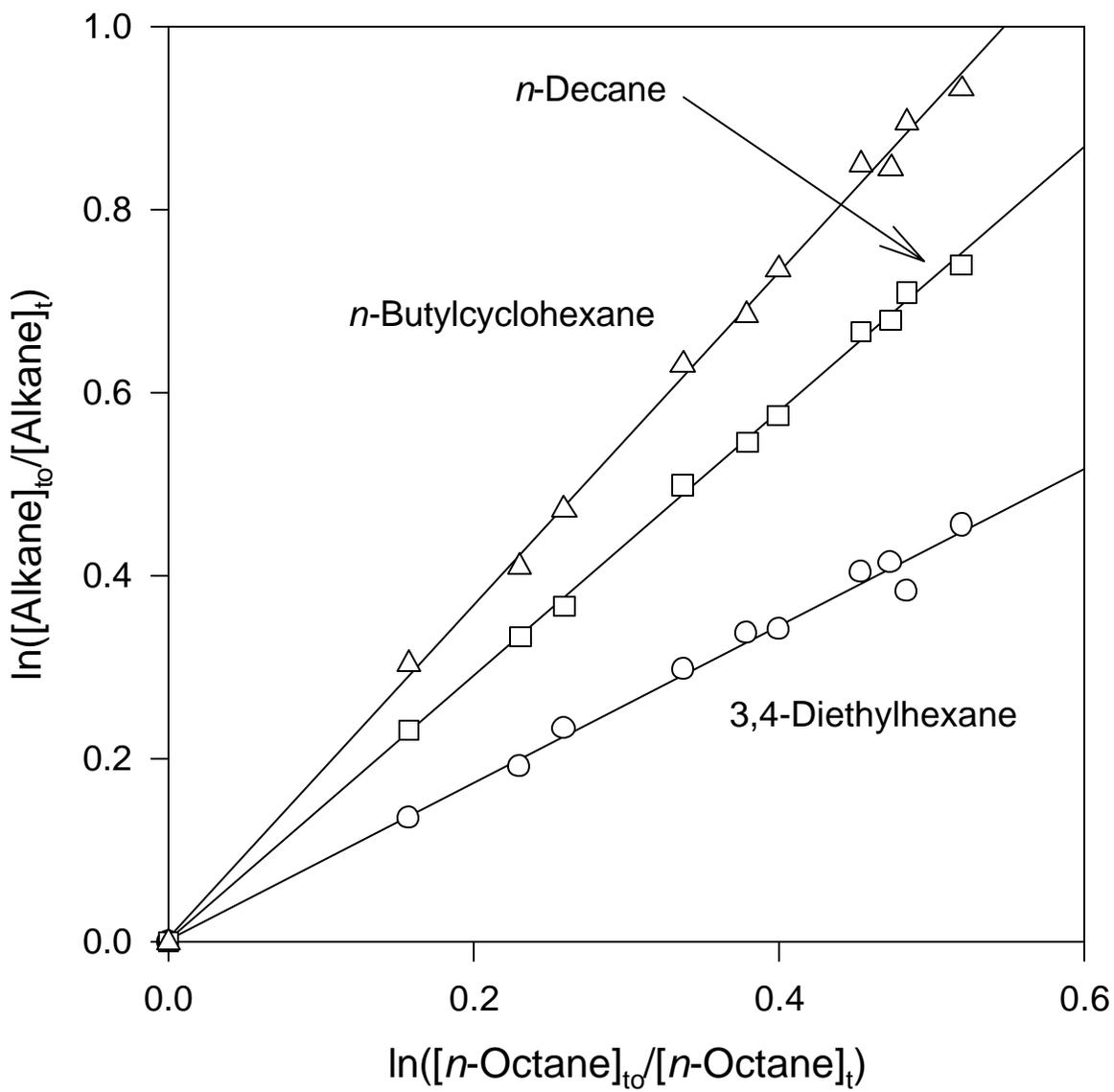


Figure 7. Plots of Equation (II) for the gas-phase reactions of OH radicals with *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane, with *n*-octane as the reference compound.

Table 5. 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  $296 \pm 2$  K.

alkane	$k_{1a}/k_{1b}$	$10^{12} \times k_{1a}$ ( $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ )		reference
		this work	literature	
<i>n</i> -decane	$1.44 \pm 0.04$	$12.5 \pm 0.4$	$11.1 \pm 0.5^c$ $11.1 \pm 0.4^d$ $12.4 \pm 0.2^e$ 11.1	Atkinson <i>et al.</i> (1982b) Nolting <i>et al.</i> (1988) Behnke <i>et al.</i> (1988) estimated <sup>f</sup>
3,4-diethylhexane	$0.857 \pm 0.055$	$7.43 \pm 0.48$	12.5	estimated <sup>f</sup>
<i>n</i> -butylcyclohexane	$1.82 \pm 0.06$	$15.8 \pm 0.6$	14.8	estimated <sup>f</sup>

<sup>a</sup>Indicated errors are two least-squares standard deviations.

<sup>b</sup>Placed on an absolute basis using a rate constant of  $k_{1b}(\text{OH} + n\text{-octane}) = 8.67 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 296 K (Atkinson, 1997a). Indicated errors do not include the uncertainties in the rate constant  $k_{1b}$ .

<sup>c</sup>At  $299 \pm 2$  K. Relative to  $k_{1b}(\text{OH} + n\text{-hexane}) = 5.54 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 299 K (Atkinson, 1997a).

<sup>d</sup>At 312 K. Relative to  $k_{1b}(\text{OH} + n\text{-heptane}) = 7.16 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 312 K (Atkinson, 1997a).

<sup>e</sup>At 300 K. Relative to  $k_{1b}(\text{OH} + n\text{-octane}) = 8.76 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  at 300 K (Atkinson, 1997a).

<sup>f</sup>At 298 K. Calculated as described by Kwok and Atkinson (1995) and Atkinson (2000b).



## Products of the OH Radical-Initiated Reactions

Irradiations of CH<sub>3</sub>ONO - NO - *n*-decane - air, CH<sub>3</sub>ONO - NO - 3,4-diethylhexane - air and CH<sub>3</sub>ONO - NO - *n*-butylcyclohexane - air mixtures were carried out, with analyses by GC-FID and GC-MS. The products observed are listed in Tables 6 (*n*-decane), 7 (3,4-diethylhexane) and 8 (*n*-butylcyclohexane). The GC-FID and GC-MS analyses showed the formation of four C<sub>10</sub> alkyl nitrates from *n*-decane. The unique MS fragmentation patterns of the *n*-alkylnitrates allowed the isomers formed from *n*-decane to be distinguished and 2-, 3-, 4-, and 5-decyl nitrate were identified. Three peaks were observed from 3,4-diethylhexane and tentatively identified from their mass spectra as the two closely eluting stereoisomers of the secondary nitrate CH<sub>3</sub>CH(ONO<sub>2</sub>)CH(C<sub>2</sub>H<sub>5</sub>)CH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> and the tertiary nitrate (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C(ONO<sub>2</sub>)CH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>. Seven closely eluting C<sub>10</sub> alkyl nitrates were identified by GC-MS from *n*-butylcyclohexane, but no isomer-specific identification was possible. These various C<sub>10</sub> alkyl nitrates were quantified by GC-FID using response factors calculated from their ECNs (see above).

The products also react with OH radicals, and these secondary reactions were taken into account as described previously (Atkinson *et al.*, 1982a). 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. The following literature rate constants (in units of 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) were used: alkanes, this work (Table 5); acetaldehyde, 15.9 (Atkinson, 1994); propanal, 19.6 (Atkinson, 1994); butanal, 23.5 (Atkinson, 1994); 3-pentanone, 2.00 (Atkinson, 1994); and cyclohexanone, 6.39 (Dagaut *et al.*, 1988). Rate constants were calculated for the various C<sub>10</sub> alkyl nitrates using the group rate constants and group substituent factors given by Atkinson (2000b), decreased by 3.6% to account for the recent reference organic recommendations of Atkinson (1997a), and were (in units of 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>): 2-decyl nitrate, 8.75; 3-decyl nitrate, 7.84; 4- and 5-decyl nitrate, 7.64 each; CH<sub>3</sub>CH(ONO<sub>2</sub>)CH(C<sub>2</sub>H<sub>5</sub>)CH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, 8.44; (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C(ONO<sub>2</sub>)CH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, 4.16; and C<sub>10</sub>-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; cyclohexanone, 1.18 for formation from *n*-butylcyclohexane; C<sub>10</sub> alkyl nitrates, 1.41 for formation from *n*-decane, 1.40 for formation from 3,4-diethylhexane, and 1.46 for formation from *n*-butylcyclohexane.

API-MS analysis of irradiated CH<sub>3</sub>ONO - NO - alkane - air mixtures were carried out using [H<sub>3</sub>O·(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup> and NO<sub>2</sub><sup>-</sup> as the reagent ions. API-MS/MS "product ion" and "precursor ion" spectra were obtained for ions observed in the API-MS spectra and the results are discussed for each of the alkanes studied below. NO<sub>2</sub><sup>-</sup> ions were used as the reagent ions to quantify the hydroxycarbonyl and hydroxynitrate products, as described under Task 1 above for the *n*-pentane through *n*-octane reactions (see also Arey *et al.*, 2001). API-MS spectra and API-MS/MS "precursor ion" spectra of the 32 u O<sub>2</sub><sup>-</sup> ion and the 46 u NO<sub>2</sub><sup>-</sup> ion showed that

Table 6. Products of the gas-phase reaction of OH radicals with *n*-decane in the presence of NO.

product	GC-FID <sup>a</sup>	API-MS
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) <sup>b</sup>
hydroxycarbonyls		observed (MW 172) <sup>b,c</sup> yield 0.22 <sup>d</sup>
hydroxynitrates		observed (MW 219) <sup>b,c</sup> yield 0.024

<sup>a</sup>Indicated errors are two least-squares standard deviations combined with estimated overall uncertainties in the GC-FID response factors for *n*-decane and products of ±5% each.

<sup>b</sup>Positive ion mode.

<sup>c</sup>Negative ion mode, as NO<sub>2</sub><sup>-</sup> adducts.

<sup>d</sup>Sum of hydroxycarbonyls (see text).

reactions of the NO<sub>2</sub><sup>-</sup> ion to form the [NO<sub>2</sub>·M]<sup>-</sup> adducts dominated over the corresponding reactions of the O<sub>2</sub><sup>-</sup> ion at NO<sub>2</sub> concentrations ≥(2-3) × 10<sup>13</sup> molecule cm<sup>-3</sup>, and that under these NO<sub>2</sub> concentration conditions the dominant ion peaks involving the hydroxycarbonyls and hydroxyalkyl nitrates were the [NO<sub>2</sub>·M]<sup>-</sup> ions. Therefore addition of NO<sub>2</sub> after the reaction was employed 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 also being introduced into the chamber. We used 5-hydroxy-2-pentanone (a 1,4-hydroxycarbonyl formed from the *n*-pentane reaction (Kwok *et al.*, 1996; Atkinson, 1997a) and the only commercially available 1,4-hydroxycarbonyl) as the internal standard for quantification of the 1,4-hydroxycarbonyl(s) formed from the C<sub>10</sub> alkanes. The hydroxyalkyl nitrate CH<sub>3</sub>CH(OH)CH(ONO<sub>2</sub>)CH<sub>3</sub> 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.* (1993) [0.037 ± 0.009] and O'Brien *et al.* (1998) [0.034 ± 0.005], as the internal standard for quantification of the 1,4-hydroxyalkyl nitrates formed.

Table 7. Products of the gas-phase reaction of OH radicals with 3,4-diethylhexane in the presence of NO.

product	GC-FID <sup>a</sup>	API-MS
acetaldehyde	0.40 <sup>b</sup>	
propanal	0.37 ± 0.06	observed <sup>c</sup>
3-pentanone	0.40 ± 0.04	observed <sup>c</sup>
3-pentyl nitrate	0.023 ± 0.011	
CH <sub>3</sub> CH(ONO <sub>2</sub> )CH(C <sub>2</sub> H <sub>5</sub> )CH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.145 ± 0.026	
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> C(ONO <sub>2</sub> )CH(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.032 ± 0.008	
total C <sub>10</sub> alkyl nitrates	0.177 ± 0.032	
hydroxycarbonyls		observed (MW 172) <sup>c</sup> yield ~0.11 <sup>d</sup>
hydroxynitrates		observed (MW 191, 219) <sup>c</sup> yield ~0.017 <sup>e</sup>

<sup>a</sup>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.

<sup>b</sup>Yield cited is the initial slope obtained from a second-order regression (see text).

<sup>c</sup>Positive ion mode.

<sup>d</sup>Negative ion mode using NO<sub>2</sub><sup>-</sup>. Ion peaks attributed to C<sub>6</sub><sup>-</sup>, C<sub>8</sub><sup>-</sup>, C<sub>9</sub><sup>-</sup> and C<sub>10</sub><sup>-</sup> hydroxycarbonyls observed; yield is the sum of these hydroxycarbonyls.

<sup>e</sup>Negative ion mode using NO<sub>2</sub><sup>-</sup>. C<sub>5</sub><sup>-</sup>, C<sub>8</sub><sup>-</sup> and C<sub>10</sub><sup>-</sup> hydroxynitrates observed; yield is the sum of these hydroxynitrates.

### *n*-Decane

GC-FID and GC-MS analyses showed the formation of 2-, 3-, 4- and 5-decyl nitrate (Table 6). Figure 8 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 6.

API-MS analysis of irradiated CH<sub>3</sub>ONO - NO - *n*-decane - air mixtures using

Table 8. Products of the gas-phase reaction of OH radicals with *n*-butylcyclohexane in the presence of NO.

product	GC-FID <sup>a</sup>	API-MS
propanal	≤0.05	
butanal	0.072 ± 0.009	observed <sup>b</sup>
cyclohexanone	0.049 ± 0.007	observed <sup>b</sup>
total C <sub>10</sub> alkyl nitrates	0.19 ± 0.06	
total hydroxycarbonyls		observed (MW 170) <sup>b</sup> yield ~0.37 <sup>c</sup>
total hydroxynitrates		observed (MW 217) <sup>b</sup> yield ~0.023 <sup>d</sup>

<sup>a</sup>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.

<sup>b</sup>Positive ion mode.

<sup>c</sup>Negative ion mode using NO<sub>2</sub><sup>-</sup>. Ion peaks attributed to C<sub>9</sub>- and C<sub>10</sub>-hydroxycarbonyls observed; yield is the sum of these hydroxycarbonyls.

<sup>d</sup>Negative ion mode using NO<sub>2</sub><sup>-</sup>. C<sub>10</sub>-hydroxynitrates observed.

[H<sub>3</sub>O·(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup> as the reagent ions showed the presence of ion peaks at 155, 171, 173, 220 and 238 u (Figure 9). API-MS/MS "product ion" and "precursor ion" spectra of these and other less intense ion peaks observed in the API-MS spectrum 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<sub>2</sub>O]<sup>+</sup>, [M+H-H<sub>2</sub>]<sup>+</sup> and [M+H]<sup>+</sup> ions of the molecular weight 172 product, and the 220 and 238 u ion peaks being the [M+H]<sup>+</sup> and [M+H<sub>3</sub>O]<sup>+</sup> 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<sub>2</sub><sup>+</sup>), and hence these molecular weight 203 and 219 products are taken to be organic nitrates. Our observations of [M+H-H<sub>2</sub>O]<sup>+</sup>, [M+H-H<sub>2</sub>]<sup>+</sup> and [M+H]<sup>+</sup> 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 (see Task 1 and Arey *et al.*, 2001). This product of molecular weight 172 is identified as a hydroxycarbonyl (presumably a 1,4-hydroxycarbonyl) of formula C<sub>10</sub>H<sub>20</sub>O<sub>2</sub>, while the molecular weight 203 and 219 products are identified as decyl nitrate(s) and hydroxydecyl nitrate(s), respectively.

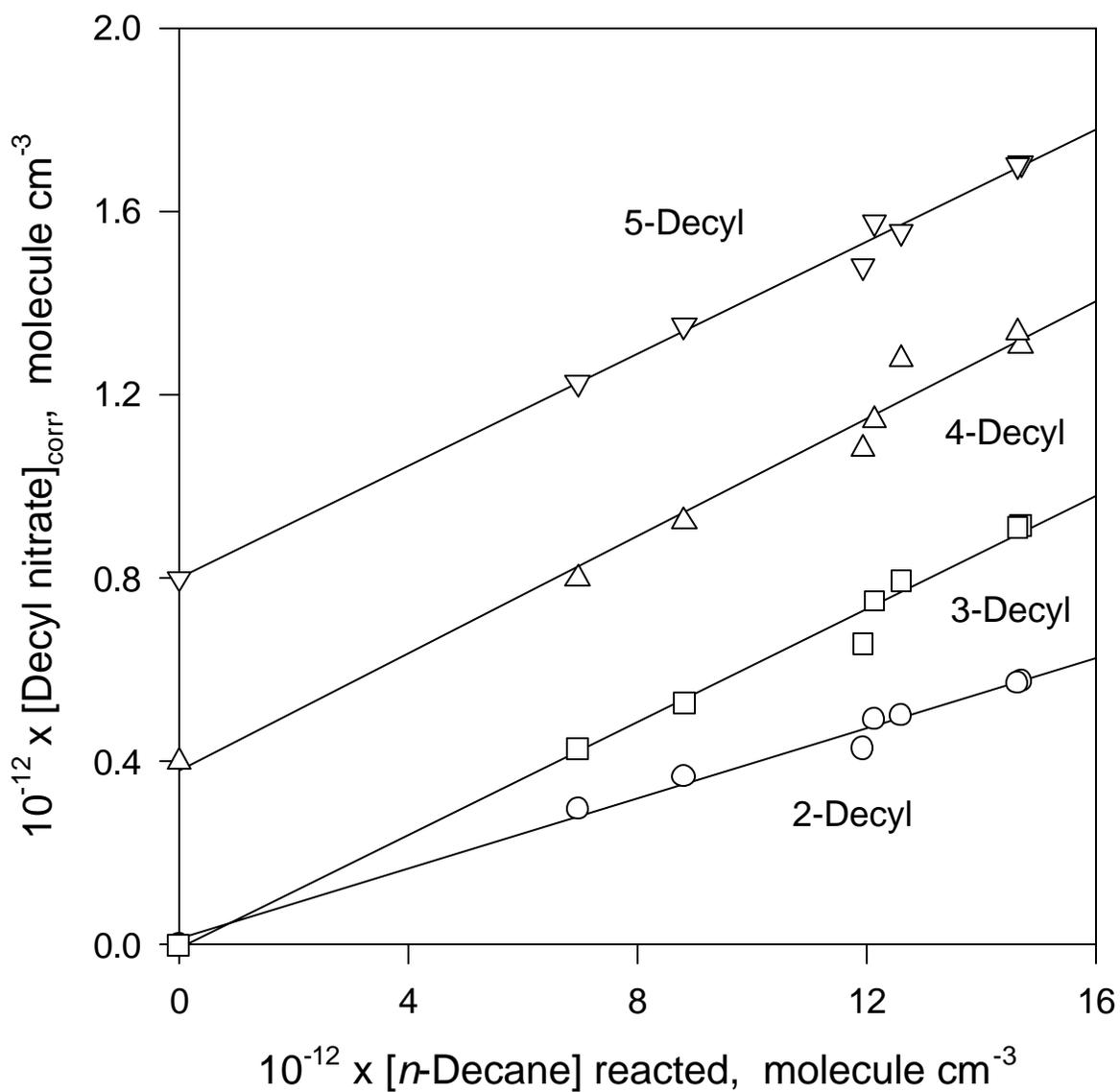


Figure 8. Plots of the amounts of 2-, 3-, 4- and 5-decyl nitrate formed, corrected for secondary reactions with OH radicals (see text), against the amounts of *n*-decane reacted with the OH radical. The data for 4- and 5-decyl nitrate have been displaced vertically by  $4.0 \times 10^{11}$  molecule  $\text{cm}^{-3}$  and  $8.0 \times 10^{11}$  molecule  $\text{cm}^{-3}$ , respectively, for clarity.

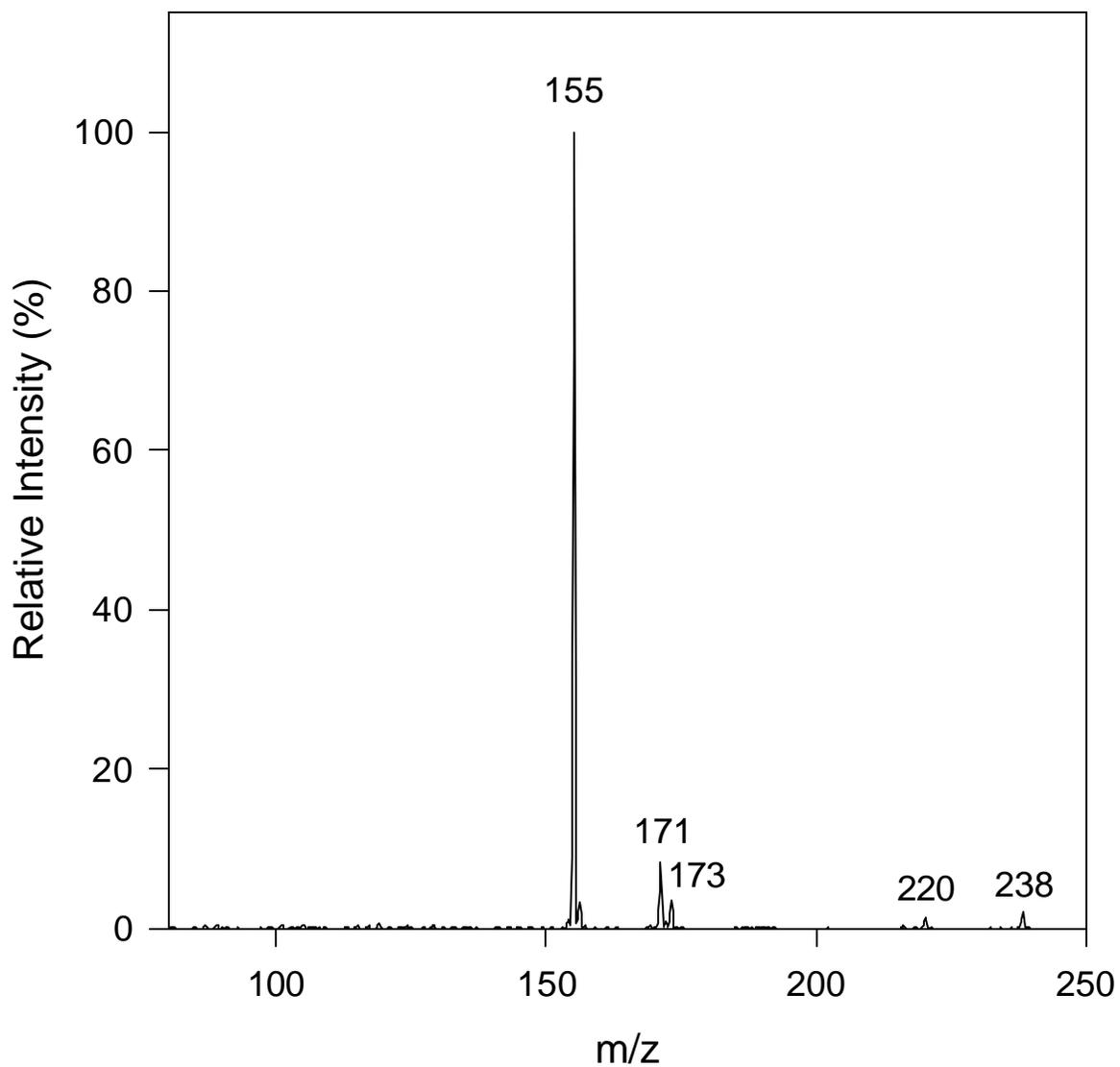


Figure 9. API-MS positive ion spectrum of an irradiated  $\text{CH}_3\text{ONO}$  -  $\text{NO}$  - *n*-decane - air mixture, using  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  as the reagent ion. See text for assignments of the observed ion peaks.

Analogous API-MS analyses of an irradiated CH<sub>3</sub>ONO - NO - *n*-decane-d<sub>22</sub> - air mixture showed the presence of ion peaks at 173, 174, 189 and 192 u, these being attributed to [M+H-HDO]<sup>+</sup>, [M+H-H<sub>2</sub>O]<sup>+</sup>, [M+H-HD]<sup>+</sup> and [M+H]<sup>+</sup> of a molecular weight 191 product, similar to our previous observations for the *n*-pentane-d<sub>12</sub> through *n*-octane-d<sub>18</sub> reactions (Kwok *et al.*, 1996).

NO<sub>2</sub><sup>-</sup> ions were also used as the reagent ions to attempt to quantify the hydroxycarbonyl and hydroxynitrate products, as described above. Figure 10 shows an API-MS spectrum of an irradiated CH<sub>3</sub>ONO - NO - *n*-decane - air mixture after addition of NO<sub>2</sub>, showing the presence of ion peaks at 218 u (NO<sub>2</sub><sup>-</sup> adduct of a molecular weight 172 species), 265 u (NO<sub>2</sub><sup>-</sup> adduct of a molecular weight 219 species) and 281 u (potentially an NO<sub>3</sub><sup>-</sup> adduct of the molecular weight 219 species). In addition to the formation of the C<sub>10</sub>-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<sub>10</sub>-hydroxycarbonyl) of C<sub>6</sub>- (15-20%), C<sub>7</sub>- (13-17%), C<sub>8</sub>- (9-15%) and C<sub>9</sub>-hydroxycarbonyls (10-15%). These observations indicate that decomposition reactions of the alkoxy and/or hydroxyalkoxy radicals must occur, although it is possible that the ion peak attributed to the NO<sub>2</sub><sup>-</sup> adduct of the C<sub>9</sub> hydroxycarbonyls was in part the O<sub>2</sub><sup>-</sup> adduct of the C<sub>10</sub> 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 6. In two of these experiments, CH<sub>3</sub>CH(OH)CH(ONO<sub>2</sub>)CH<sub>3</sub> 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, as described above. The hydroxydecyl nitrate formation yield resulting from these experiments is also given in Table 6. As noted previously (see discussion for Task 1 above), the API-MS is quite sensitive to hydroxyalkyl nitrates (more so than to hydroxycarbonyls, as evident from Figure 10 and the formation yields given in Table 6).

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 (Kwok and Atkinson, 1995; Atkinson, 2000b). Hence the 2-, 3-, 4- and 5-decyl nitrate yields from their precursor secondary C<sub>10</sub>O<sub>2</sub><sup>•</sup> 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<sub>2</sub> groups, the average secondary decyl nitrate yield from secondary C<sub>10</sub>O<sub>2</sub><sup>•</sup> radicals is 0.233 ± 0.040. This decyl nitrate yield per secondary RO<sub>2</sub><sup>•</sup> radical is ~15% lower than the value of 0.27 expected for a secondary C<sub>10</sub>O<sub>2</sub><sup>•</sup> radical (see Task 1 above and Arey *et al.*, 2001). Because of the rapid isomerization of all of the initially-formed alkoxy radicals in the *n*-decane reaction (Atkinson, 1997a,b) [see also below], formation of decyl nitrates from the reaction



was of no importance for the experimental conditions employed here.

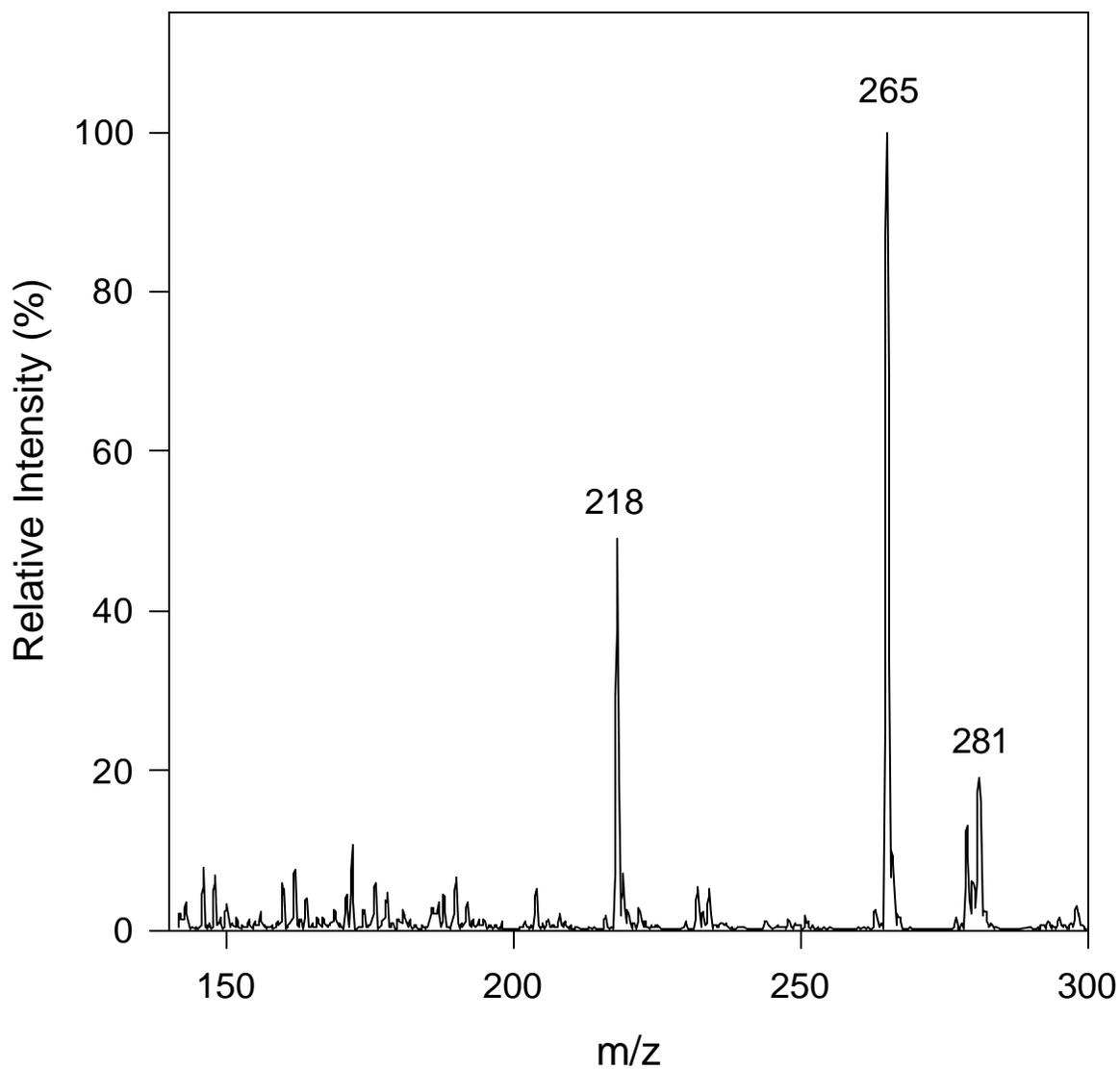


Figure 10. API-MS negative ion spectrum of an irradiated  $\text{CH}_3\text{ONO}$  -  $\text{NO}$  - *n*-decane - air mixture, using  $\text{NO}_2^-$  as the reagent ion. See text for assignments of the observed ion peaks.

The product formation yields listed in Table 6 account for 47% of the reaction products from *n*-decane. However, it must be noted that the hydroxycarbonyl and hydroxynitrate yields given in Table 6 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<sub>10</sub>- 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 noted by reactions (1)-(3) of the Introduction, 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<sub>10</sub>-alkoxy radicals can react with O<sub>2</sub>, decompose by C-C bond scission, or isomerize through a six-membered transition state to form 1,4-hydroxydecyl radicals (Atkinson, 1997a,b).



The empirical estimation method of Aschmann and Atkinson (1999) predicts that at 298 K and atmospheric pressure of air the isomerization rate for all of the decoxy radicals are  $\sim 2.6 \times 10^6 \text{ s}^{-1}$ , a factor of ~40 higher than the estimated rates of the O<sub>2</sub> reactions ( $\sim 5 \times 10^4 \text{ s}^{-1}$ ) and decompositions ( $\sim 1 \times 10^4 \text{ s}^{-1}$ ). The 1,4-hydroxydecyl radicals formed from the isomerization reactions then add O<sub>2</sub> to form 1,4-hydroxydecyl peroxy radicals, which react with NO to form 1,4-hydroxydecyl nitrates [RCH(OH)CH<sub>2</sub>CH<sub>2</sub>CH(ONO<sub>2</sub>)R'] or 1,4-hydroxydecoxy radicals [RCH(OH)CH<sub>2</sub>CH<sub>2</sub>CH(O<sup>•</sup>)R'] plus NO<sub>2</sub> [by reactions analogous to reactions (2) and (3)]. The 1,4-hydroxydecoxy radicals react with O<sub>2</sub>, decompose by C-C bond scission, or isomerize, with the isomerization reaction



being estimated to be even more rapid than the initial isomerization, with a rate of  $\sim 2 \times 10^7 \text{ s}^{-1}$  (and hence dominating over the decomposition and O<sub>2</sub> reactions by a factor of  $>10^2$ ). The resulting  $\alpha$ -hydroxy radical reacts with O<sub>2</sub> to form the 1,4-hydroxycarbonyl.



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, and thereby analogous to our conclusions in Task 1 for the corresponding *n*-hexane through *n*-octane reactions (see also Kwok *et al.*, 1996; Arey *et al.*, 2001).

### 3,4-Diethylhexane

GC-FID and GC-MS analyses of irradiated CH<sub>3</sub>ONO - NO - 3,4-diethylhexane - air mixtures showed the formation of acetaldehyde, propanal, 3-pentanone, and (tentatively) the C<sub>10</sub>-alkyl nitrates CH<sub>3</sub>CH(ONO<sub>2</sub>)CH(C<sub>2</sub>H<sub>5</sub>)CH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> and (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>C(ONO<sub>2</sub>)CH(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>. In addition, a small GC peak was observed with a retention time matching that of 3-pentyl nitrate. Figure 11 shows plots of the amounts of selected products formed, corrected for secondary reactions, against the amounts of 2,3-diethylhexane reacted, and the product formation yields obtained from least-squares analyses of these data are given in Table 7. The plot of the amount of acetaldehyde formed against the amount of 3,4-diethylhexane reacted (Figure 11) 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 (Atkinson, 1994, 2000a) 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 7 and is taken to be the yield of acetaldehyde as a first-generation product.

API-MS analyses of irradiated CH<sub>3</sub>ONO - NO - 3,4-diethylhexane - air mixtures, using [H<sub>3</sub>O·(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup> ions showed the presence of significant ion peaks at 87, 105, 155, 171, 173 and 306 u (Figure 12), 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]<sup>+</sup> and [M+H<sub>3</sub>O]<sup>+</sup> ions of the molecular weight 86 product (attributed to 3-pentanone), the ion peaks at 155, 171 and 173 being the [M+H-H<sub>2</sub>O]<sup>+</sup>, [M+H-H<sub>2</sub>]<sup>+</sup> and [M+H]<sup>+</sup> 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 heterodimer of the molecular weight 86 and 191 products, the 238 u ion peak being the [M+H<sub>3</sub>O]<sup>+</sup> 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 7), as a product in the API-MS analyses was determined by MS/MS analysis of the 203 u ion peak which is attributed to a protonated heterotrimer of two molecules of propanal plus pentanone. Analogous to the *n*-decane reaction system, the molecular weight 172 and 219 products are attributed to a hydroxycarbonyl of formula C<sub>10</sub>H<sub>19</sub>(OH)(O) and a hydroxynitrate of formula C<sub>10</sub>H<sub>20</sub>(OH)(ONO<sub>2</sub>).

NO<sub>2</sub><sup>-</sup> ions were also used as the reagent ion to quantify the hydroxycarbonyl and hydroxynitrate products. Figure 13 shows an API-MS spectrum of an irradiated CH<sub>3</sub>ONO - NO - 3,4-diethylhexane - air mixture after addition of NO<sub>2</sub>, showing 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<sub>2</sub><sup>-</sup> adducts of molecular weight 149, 191 and 219 species, and with the 281 u ion peak potentially being an NO<sub>3</sub><sup>-</sup> adduct of the molecular weight 219 species. The molecular weight

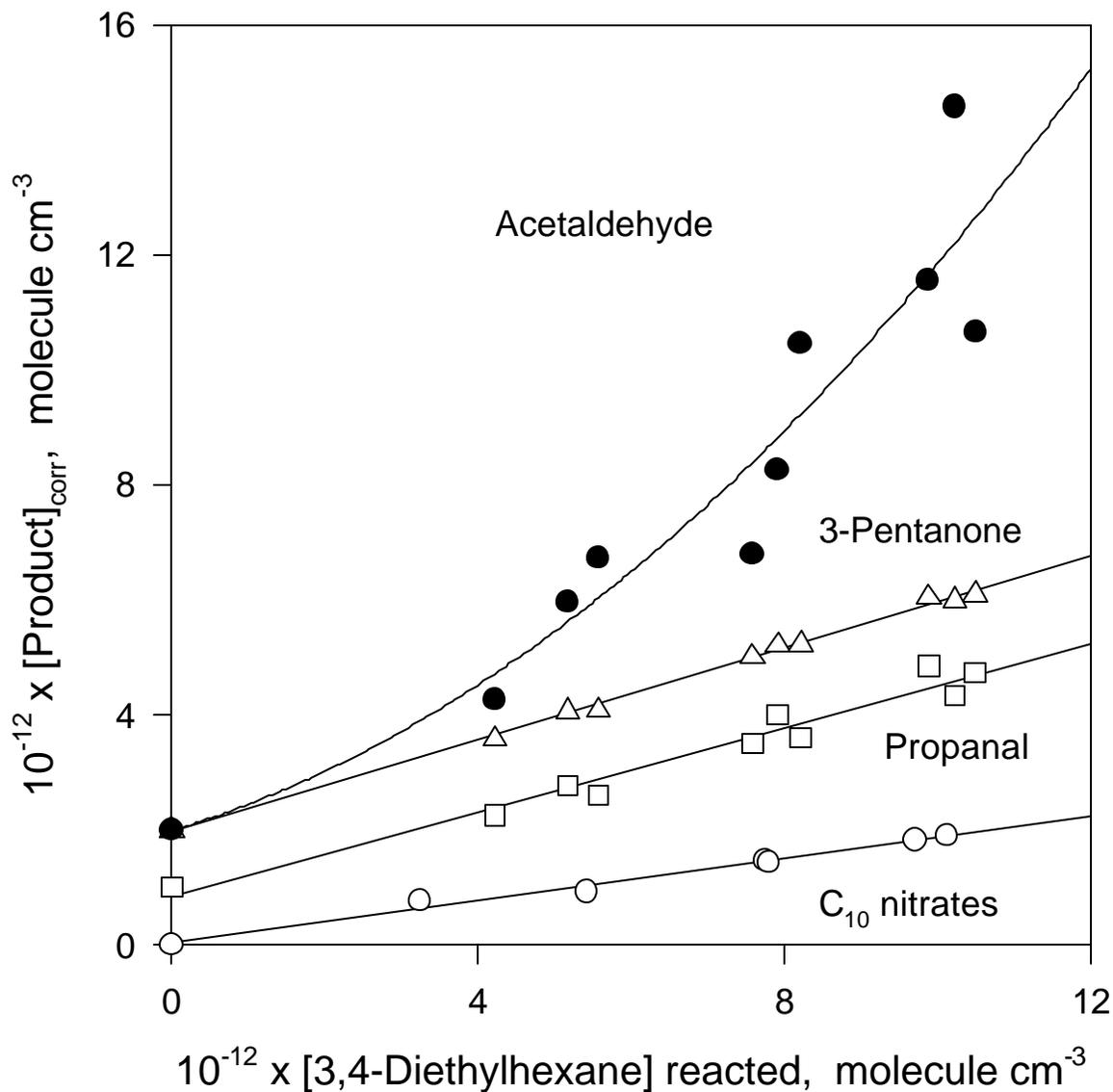


Figure 11. Plots of the amounts of  $\text{C}_{10}$  nitrates, propanal, 3-pentanone and acetaldehyde formed, corrected for secondary reactions with OH radicals (see text), against the amounts of 3,4-diethylhexane reacted with the OH radical. The data for propanal, 3-pentanone and acetaldehyde have been displaced vertically by  $1.0 \times 10^{12}$  molecule  $\text{cm}^{-3}$ ,  $2.0 \times 10^{12}$  molecule  $\text{cm}^{-3}$  and  $2.0 \times 10^{12}$  molecule  $\text{cm}^{-3}$ , respectively, for clarity. The line through the acetaldehyde data is from a second-order regression (see text).

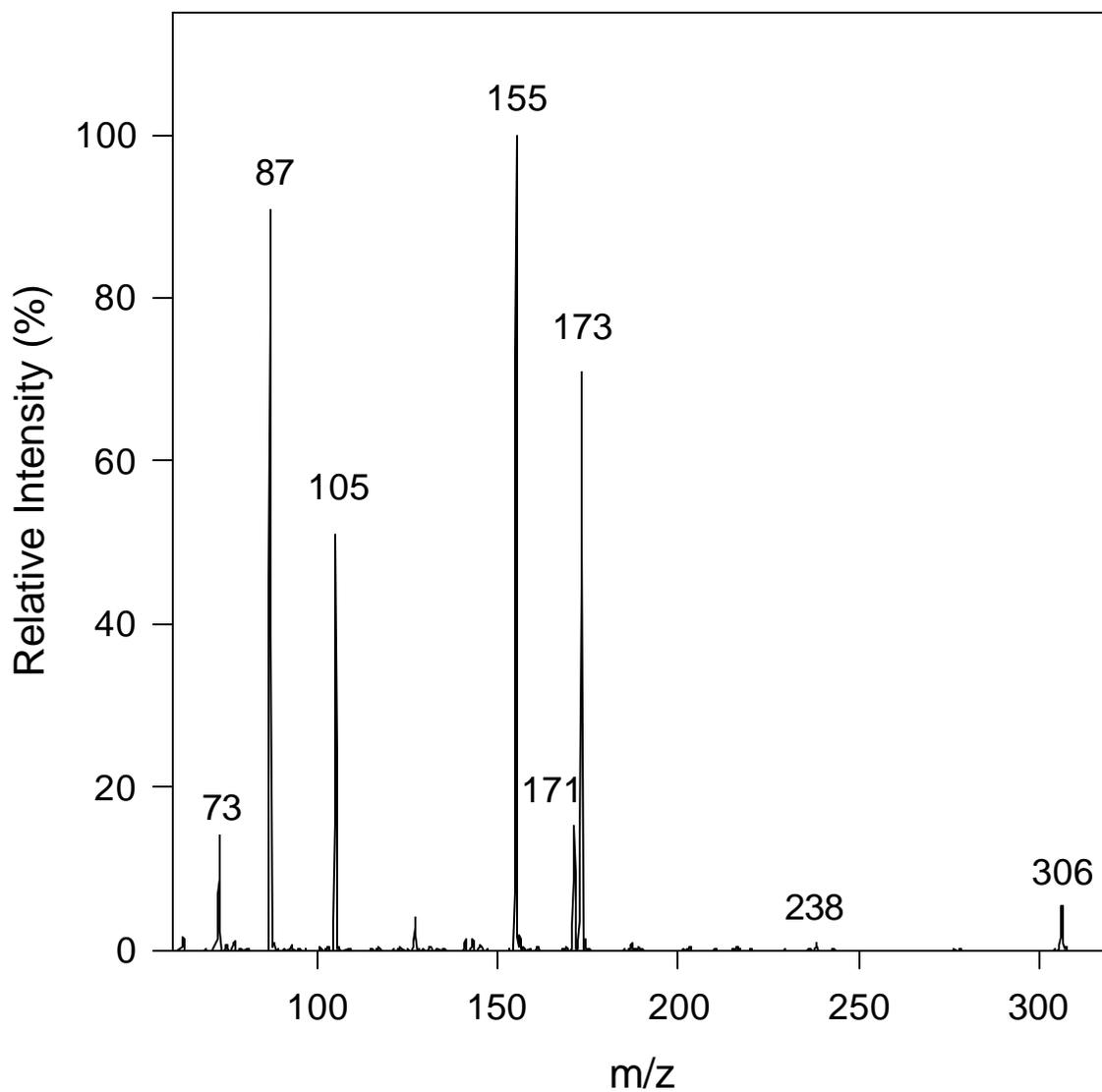


Figure 12. API-MS positive ion spectrum of an irradiated  $\text{CH}_3\text{ONO} - \text{NO} - 3,4\text{-diethylhexane} - \text{air}$  mixture, using  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  as the reagent ion. See text for assignments of the observed ion peaks.

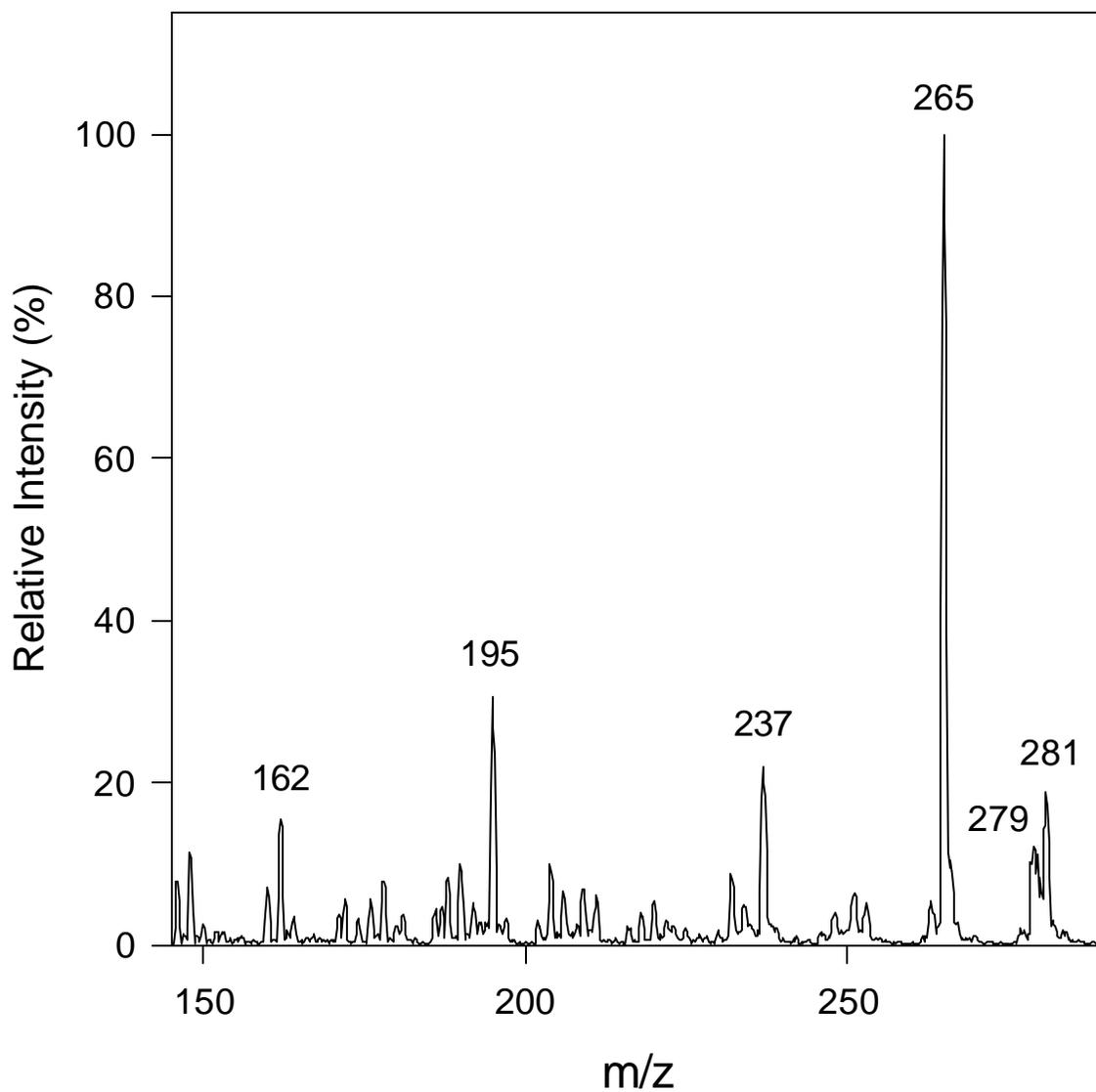


Figure 13. API-MS negative ion spectrum of an irradiated  $\text{CH}_3\text{ONO} - \text{NO} - 3,4\text{-diethylhexane} - \text{air}$  mixture, using  $\text{NO}_2^-$  as the reagent ion. See text for assignments of the observed ion peaks.

149 and 191 species are attributed to C<sub>5</sub>- and C<sub>8</sub>-hydroxynitrates. The API-MS spectra (such as that shown in Figure 13) show that ion peaks arising from hydroxycarbonyls [at 190 (NO<sub>2</sub><sup>-</sup> adduct of a C<sub>8</sub>-hydroxycarbonyl), 204 (NO<sub>2</sub><sup>-</sup> adduct of a C<sub>9</sub>-hydroxycarbonyl) and 232 (NO<sub>3</sub><sup>-</sup> adduct of a C<sub>10</sub>-hydroxycarbonyl)] were of low intensity. Experiments were carried out with 5-hydroxy-2-pentanone being added as the internal standard after the irradiation, and the resulting yield data of hydroxycarbonyls from the 3,4-diethylhexane reaction are given in Table 7. In two of these experiments, CH<sub>3</sub>CH(OH)CH(ONO<sub>2</sub>)CH<sub>3</sub> 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. The hydroxynitrate formation yield resulting from these experiments is also given in Table 7.

It is calculated that the fractions of the initial OH radical reaction proceeding by H-atom abstraction from the CH<sub>3</sub>, CH<sub>2</sub> and CH groups are 5.4%, 36.8% and 57.8%, respectively (Kwok and Atkinson, 1995), 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 5). Reactions (1) through (3) lead to the formation of primary, secondary and tertiary C<sub>10</sub> alkyl nitrates

O<sub>2</sub>NOCH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>2</sub>CH<sub>3</sub>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, CH<sub>3</sub>CH(ONO<sub>2</sub>)CH(CH<sub>2</sub>CH<sub>3</sub>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> and (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C(ONO<sub>2</sub>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> [of molecular weight 219], or NO<sub>2</sub> plus the alkoxy radicals (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>CHCH(CH<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>O<sup>•</sup>, CH<sub>3</sub>CH(O<sup>•</sup>)CH(CH<sub>2</sub>CH<sub>3</sub>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>, and (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C(O<sup>•</sup>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>.

It is estimated (Aschmann and Atkinson, 1999) that decomposition of the (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C(O<sup>•</sup>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> radical



dominates over isomerization at 298 K by a factor of 10<sup>2</sup>, with the 3-pentyl radical reacting to form 3-pentyl nitrate (12.6%), 3-pentanone (52%), and acetaldehyde plus propanal (35%), where the percentage yields in parentheses are from Atkinson *et al.* (1995a) and Arey *et al.* (2001).

It is also estimated that the CH<sub>3</sub>CH(O<sup>•</sup>)CH(CH<sub>2</sub>CH<sub>3</sub>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> radical will mainly undergo primarily isomerization (4.2 x 10<sup>6</sup> s<sup>-1</sup>) and decomposition (2.2 x 10<sup>6</sup> s<sup>-1</sup>). The isomerization pathway is expected to form mainly the C<sub>10</sub> hydroxycarbonyl CH<sub>3</sub>CH(O)CH(CH<sub>2</sub>CH<sub>3</sub>)CH(CH<sub>2</sub>CH<sub>3</sub>)CH(OH)CH<sub>3</sub> (see results of the *n*-decane reaction system, above). The alkoxy radical CH<sub>3</sub>CH<sub>2</sub>CH(O<sup>•</sup>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> formed from the decomposition reaction (14)



is predicted to react mainly (85%) via decomposition [reaction (15)] to yield propanal and the 3-pentyl radical (which, as noted above, reacts to form 3-pentyl nitrate, acetaldehyde, propanal and 3-pentanone), and by isomerisation [reaction (16)].





The hydroxyalkyl radical formed in reaction (16) is anticipated to react by a sequence of reactions, including a second isomerization, to form the C<sub>8</sub>-hydroxycarbonyl CH<sub>3</sub>CH<sub>2</sub>C(O)CH(CH<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>OH and the C<sub>8</sub>-hydroxynitrate CH<sub>3</sub>CH<sub>2</sub>CH(OH)CH(CH<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>ONO<sub>2</sub>.

The primary alkoxy radical (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>CHCH(CH<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>O<sup>•</sup> is predicted to undergo almost exclusively isomerization leading to (after reaction of the resulting hydroxyalkyl radical with O<sub>2</sub> and then NO) mainly the (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C(O<sup>•</sup>)CH(CH<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>OH radical, which is predicted to decompose (84% of the time) rather than undergo another isomerization to ultimately form (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C(OH)CH(CH<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>CHO.



Further reactions of the 1-hydroxy-3-pentyl radical are expected to lead to the formation of 1-hydroxy-3-pentanone, propanal plus glycolaldehyde, or propanal + HCHO + HCHO.

Our product data are in reasonable accord with these expectations. Based on our measured 3-pentanone yield, and taking into account formation of the tertiary nitrate and assuming formation of 3-pentanone only from reaction (13), 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<sub>3</sub>CH<sub>2</sub>CH(O<sup>•</sup>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> 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. 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, 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<sub>10</sub> alkyl nitrate yields (Table 7), then the percentages of the C<sub>10</sub> alkoxy radicals formed are 9% (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>CHCH(CH<sub>2</sub>CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>O<sup>•</sup> radicals, 47% CH<sub>3</sub>CH(O<sup>•</sup>)CH(CH<sub>2</sub>CH<sub>3</sub>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> radicals and 26% (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C(O<sup>•</sup>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> radicals. The subsequent reactions of these alkoxy radicals are predicted 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<sub>2</sub>CH<sub>2</sub>O<sup>•</sup> radical formed from the exothermic HOCH<sub>2</sub>CH<sub>2</sub>OO<sup>•</sup> + NO reaction, where decomposition is enhanced over that for HOCH<sub>2</sub>CH<sub>2</sub>O<sup>•</sup> radicals formed from the approximately thermoneutral peroxy + peroxy radical reaction, it is possible that decomposition of the (CH<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C(O<sup>•</sup>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> radical to 3-pentanone plus 3-pentyl radical (which is estimated to be slightly exothermic) 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<sub>2</sub> 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<sub>3</sub>CH<sub>2</sub>)<sub>2</sub>C(O<sup>•</sup>)CH(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub> 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  $(\text{CH}_3\text{CH}_2)_2\text{C}(\text{O}^\bullet)\text{CH}(\text{CH}_2\text{CH}_3)_2$  radical preferentially decomposes rather than reacting with  $\text{O}_2$ .

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  $\text{C}_{10}$  alkyl nitrates from their precursor  $\text{RO}_2^\bullet$  radicals are  $\sim 0.24$  and  $\sim 0.11$ , respectively, consistent with an expected formation yield of  $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}(\text{CH}_2\text{CH}_3)_2$  from its precursor  $\text{C}_{10}\text{H}_{21}\text{O}_2^\bullet$  radical of  $\sim 27\%$  (Arey *et al.*, 2001) and a significantly lower yield of  $(\text{CH}_3\text{CH}_2)_2\text{C}(\text{ONO}_2)\text{CH}(\text{CH}_2\text{CH}_3)_2$  from its precursor tertiary  $\text{C}_{10}\text{H}_{21}\text{O}_2^\bullet$  radical (Carter and Atkinson, 1989). The products identified and quantified by gas chromatography account for  $\sim 60\%$  of the reaction pathways. The majority of the remaining products are predicted to be  $\text{C}_5$ -,  $\text{C}_8$ - and  $\text{C}_{10}$ -hydroxycarbonyls and hydroxynitrates, which our API-MS analyses indicate account for an additional  $\sim 13\%$  (uncertain to a factor of 2-3) of the overall products.

### *n*-Butylcyclohexane

GC-FID and GC-MS analyses of irradiated  $\text{CH}_3\text{ONO} - \text{NO} - n$ -butyl cyclohexane - air mixtures showed the formation of butanal, cyclohexanone, and seven closely eluting  $\text{C}_{10}$ -alkyl nitrates (with no isomer-specific identifications). These GC analyses showed no evidence for the formation of propanal. The  $\text{C}_{10}$  alkyl nitrates were quantified by GC-FID using response factors calculated using their ECNs (see above). Figure 14 shows plots of the amounts of selected products formed, corrected for secondary reactions, against the amounts of *n*-butylcyclohexane reacted, and the product formation yields obtained from least-squares analyses of these data are given in Table 8.

API-MS analysis of irradiated  $\text{CH}_3\text{ONO} - \text{NO} - n$ -butylcyclohexane - air mixtures using  $[\text{H}_3\text{O} \cdot (\text{H}_2\text{O})_n]^\bullet$  as the reagent ion showed the presence of product ion peaks at 99, 117, 153, 169, 171, 185, 218 and 236 u (Figure 15). API-MS/MS "product ion" and "precursor ion" spectra indicated that these were due to products of molecular weight 98, 170, and 217, with the observed ion peaks at 99 and 117 u being the  $[\text{M}+\text{H}]^+$  and  $[\text{M}+\text{H}_3\text{O}]^+$  ions of the molecular weight 98 product (attributed to cyclohexanone), the ion peaks at 153, 169 and 171 being the  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$ ,  $[\text{M}+\text{H}-\text{H}_2]^\bullet$  and  $[\text{M}+\text{H}]^\bullet$  of the molecular weight 170 product, and the 218 u and 236 u ion peaks being, respectively, the  $[\text{M}+\text{H}]^\bullet$  and  $[\text{M}+\text{H}_3\text{O}]^\bullet$  of the molecular weight 217 product. The API-MS/MS "product ion" spectrum of the 218 u ion peak shown in Figure 16 exhibiting an intense fragment at 46 u ( $\text{NO}_2^+$ ), is attributed to an organic

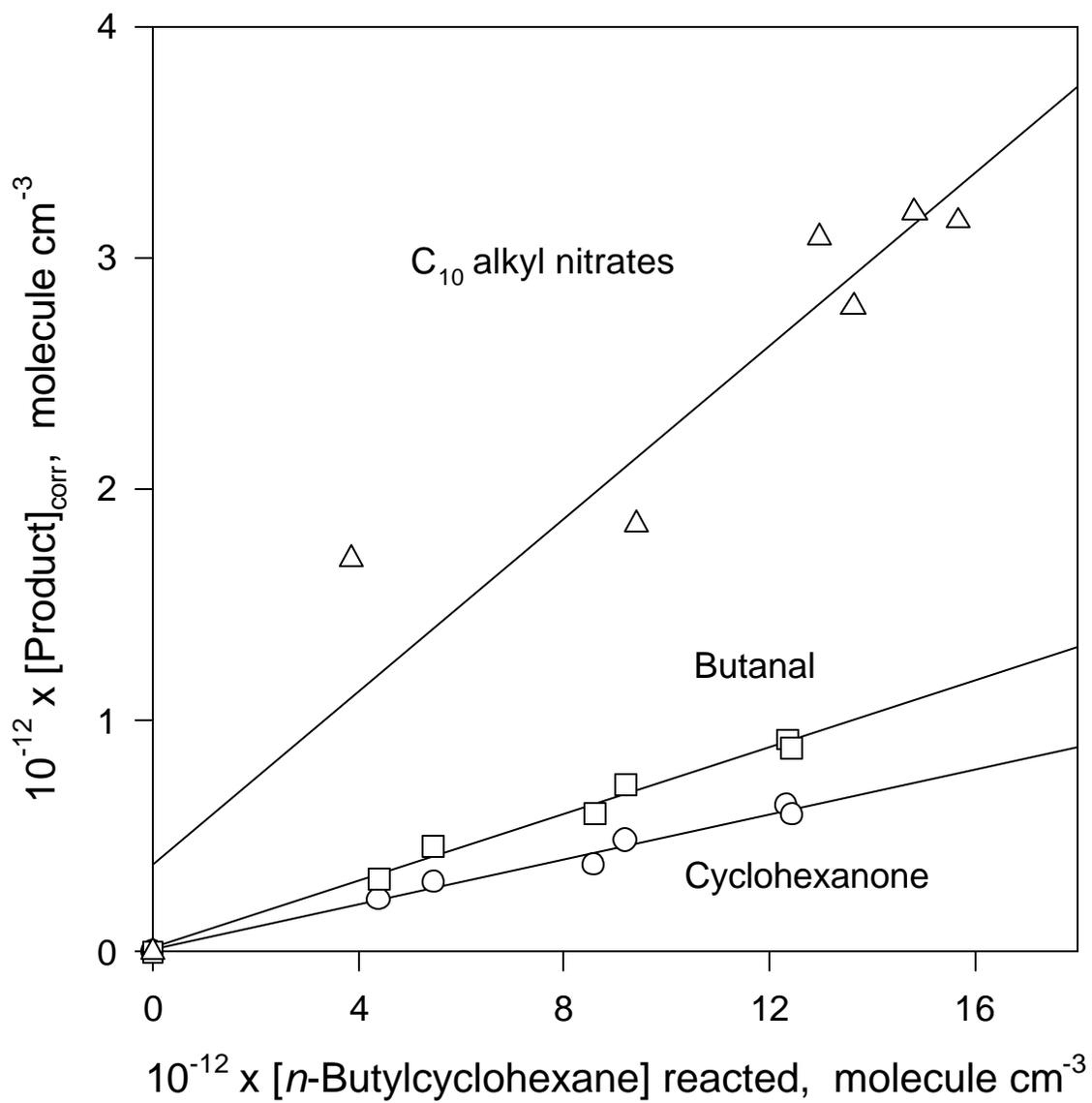
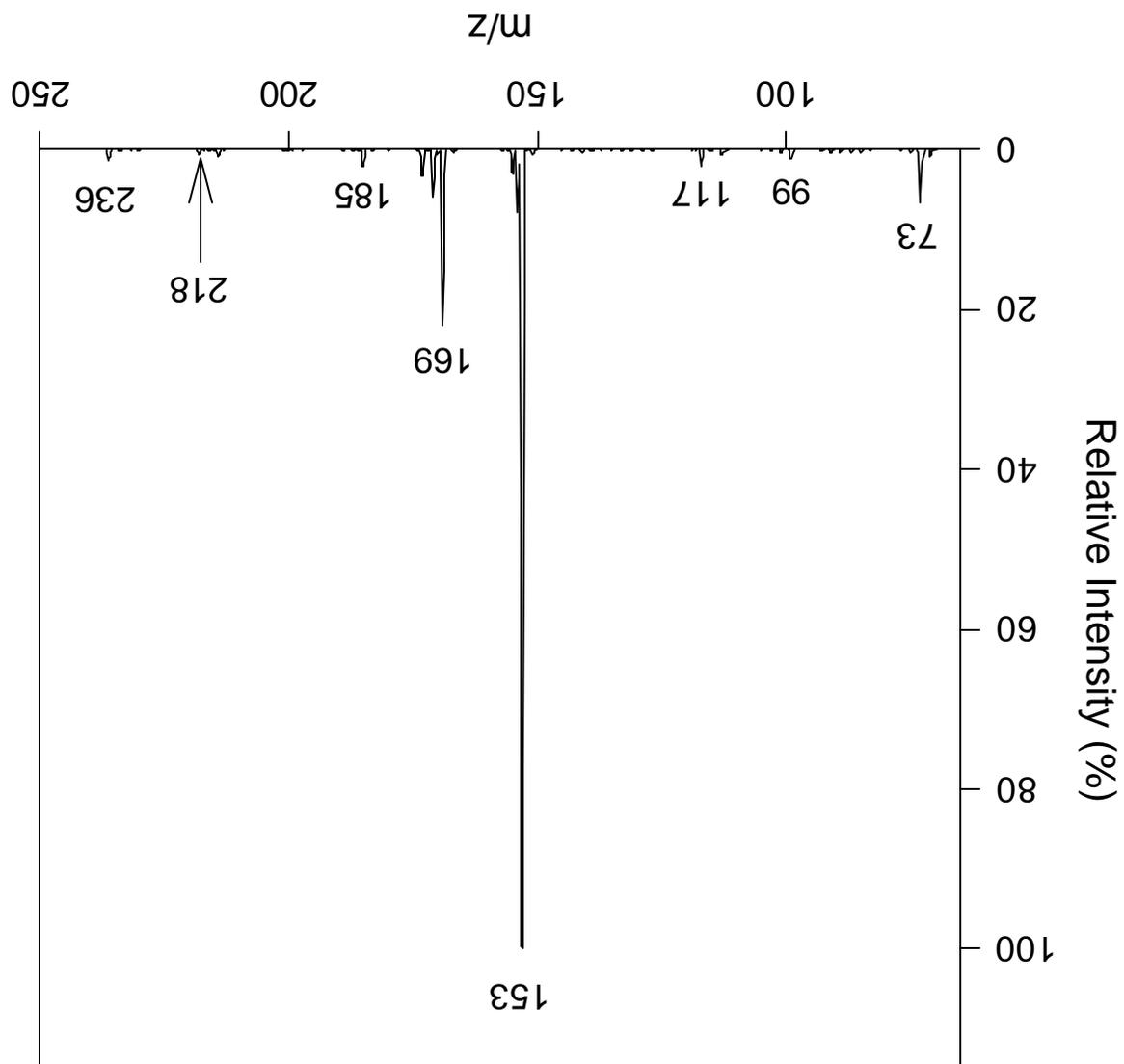


Figure 14. Plots of the amounts of  $C_{10}$  nitrates, butanal and cyclohexanone formed, corrected for secondary reactions with OH radicals (see text), against the amounts of *n*-butylcyclohexane reacted with the OH radical.

Figure 15. API-MS positive ion spectrum of an irradiated  $\text{CH}_3\text{ONO} - \text{NO} - n\text{-butylcyclohexane}$  - air mixture, using  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  as the reagent ion. See text for assignments of the observed ion peaks.



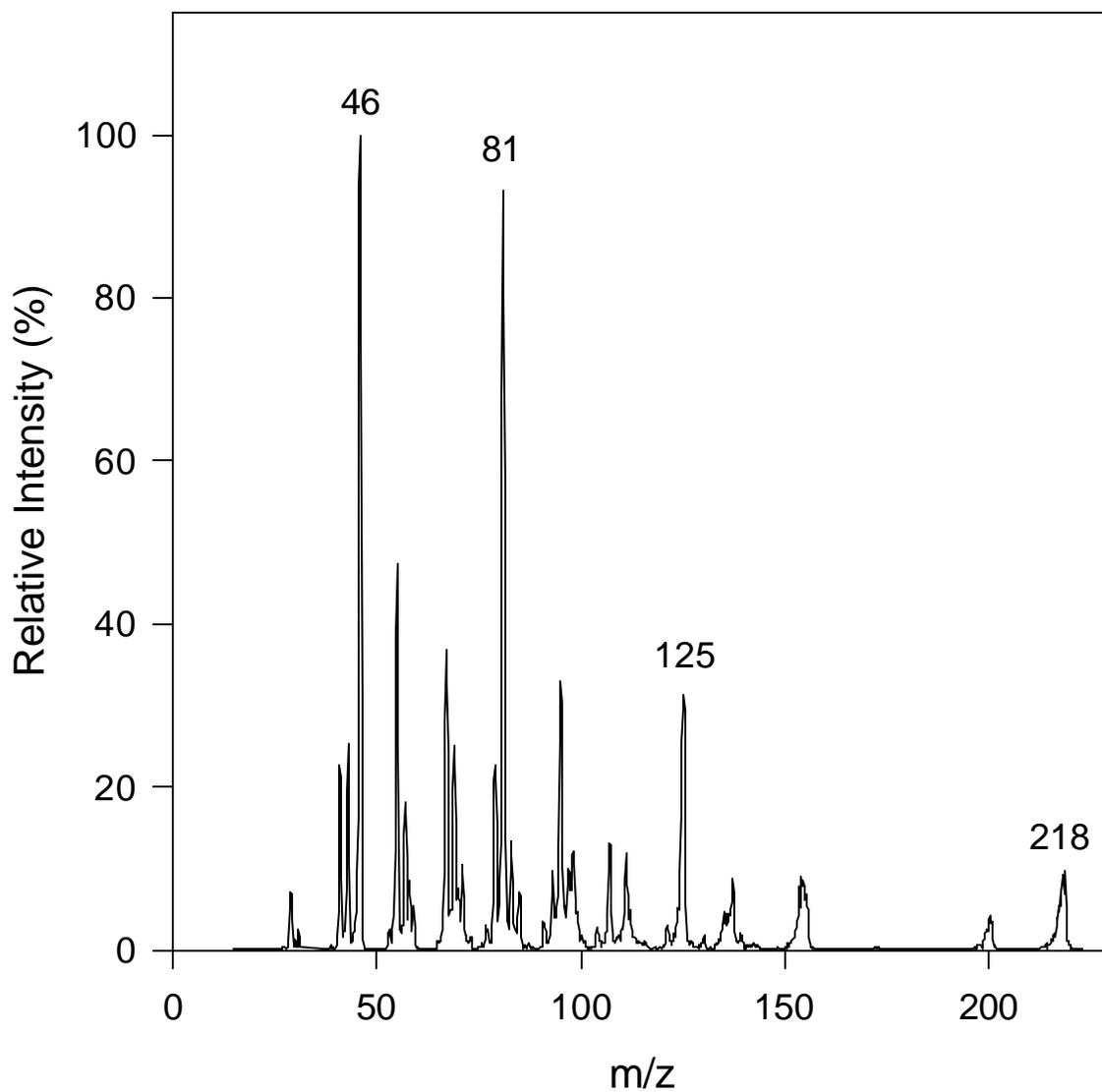


Figure 16. API-MS/MS CAD "product ion" spectrum of the 218 u ion peak observed in irradiated  $\text{CH}_3\text{ONO} - \text{NO} - n\text{-butylcyclohexane} - \text{air}$  irradiations, using  $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$  as the reagent ions.

nitrate. As discussed below, the molecular weight 170 product is attributed to a hydroxycarbonyl and/or dicarbonyl of formula  $C_{10}H_{18}O_2$ , while the molecular weight 217 product is attributed to a hydroxynitrate and/or carbonylnitrate of formula  $C_{10}H_{19}O(ONO_2)$ .

$NO_2^-$  ions were also used as the reagent ion to quantify the hydroxycarbonyl and hydroxynitrate products. Figure 17 shows an API-MS spectrum of an irradiated  $CH_3ONO - NO - n$ -butylcyclohexane - air mixture after addition of  $NO_2$ , showing 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 being added as the internal standard after the irradiation, and the yield of hydroxycarbonyls from the *n*-butylcyclohexane reaction is given in Table 8. 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 and used as an internal standard for hydroxyalkyl nitrate quantification. The hydroxydecyl nitrate formation yield resulting from these experiments is also given in Table 8. It is estimated 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 (1999), then it is expected that the alkoxy radicals  $CH_3CH(O^{\bullet})CH_2CH_2$ -cyc- $C_6H_{11}$ ,  $CH_3CH_2CH(O^{\bullet})CH_2$ -cyc- $C_6H_{11}$  and 1-butyl-1-cyclohexoxy will dominantly isomerize, to ultimately form molecular weight 170 hydroxycarbonyls. In contrast, the  $CH_3CH_2CH_2CH(O^{\bullet})$ -cyc- $C_6H_{11}$  radical is predicted to decompose



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  $HC(O)CH_2CH(OH)CH_2CH_2CHO$  (Aschmann *et al.*, 1997; Platz *et al.*, 1999; Orlando *et al.*, 2000). The predicted yields of the observed products butanal and cyclohexanone are therefore 7.7% and 2.5%, respectively, assuming an alkyl nitrate yield of 19% from the secondary  $C_{10}O_2^{\bullet}$  radical. This predicted butanal yield is close to that measured ( $7.2 \pm 0.9\%$ ), while the measured cyclohexanone yield of  $4.9 \pm 0.7\%$  is a factor of 2 higher than the predicted value, implying other small source(s) of cyclohexanone. These could include formation of cyclohexanone from the predicted dominant isomerization of the  $O^{\bullet}CH_2CH_2CH_2CH_2$ -cyc- $C_6H_{11}$  radical to form the  $HOCH_2CH_2CH_2CH(O^{\bullet})$ -cyc- $C_6H_{11}$  alkoxy radical, which can either decompose [to  $HOCH_2CH_2CH_2CHO$  plus cyclohexyl] or isomerize, with these processes being estimated to be competitive ( $3.8 \times 10^6 \text{ s}^{-1}$  and  $9 \times 10^6 \text{ s}^{-1}$  at 298 K, respectively), and with the cyclohexyl radical forming in part cyclohexanone (see above).

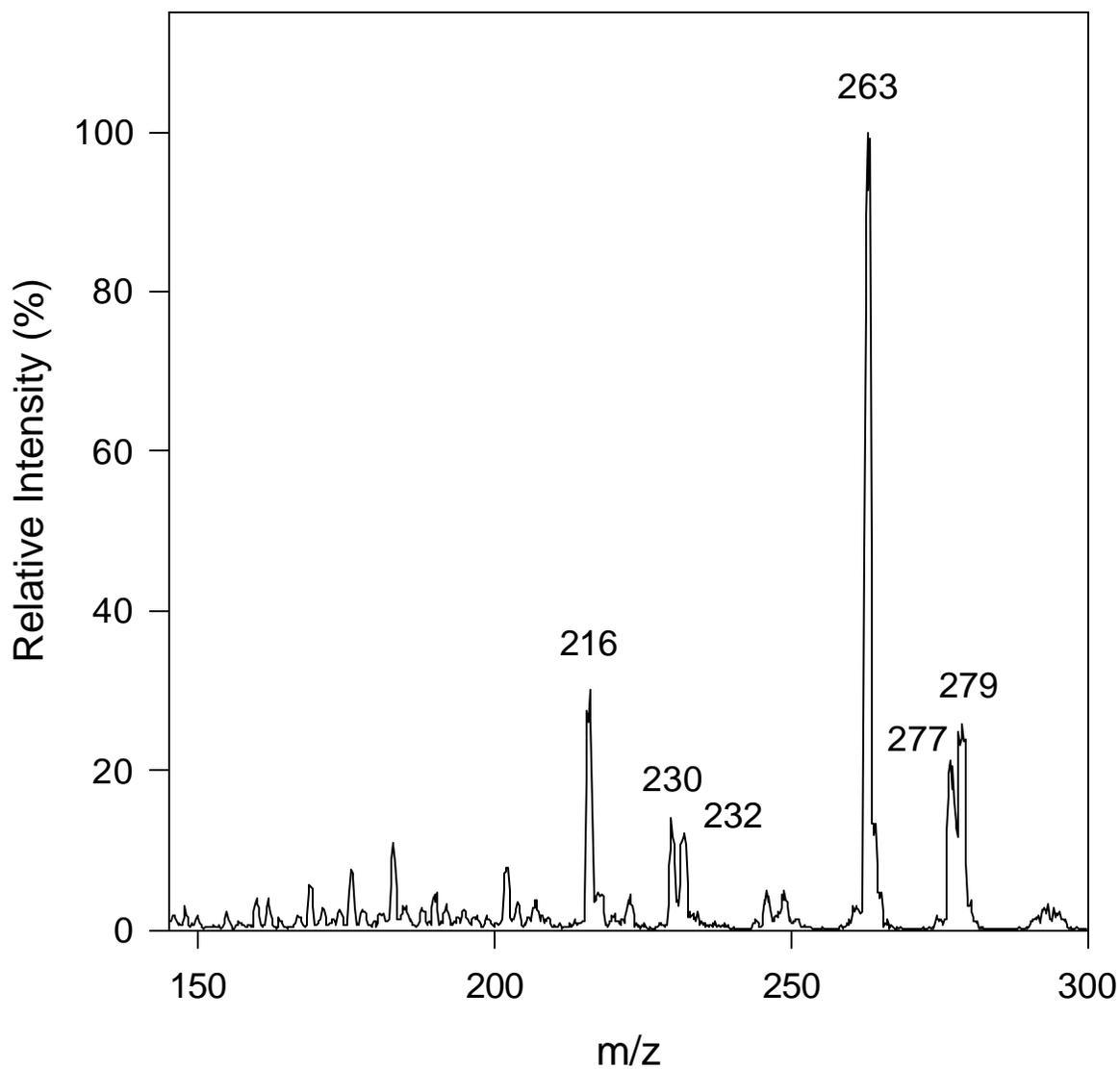


Figure 17. API-MS negative ion spectrum of an irradiated  $\text{CH}_3\text{ONO} - \text{NO} - n\text{-butylcyclohexane} - \text{air}$  mixture, using  $\text{NO}_2^-$  as the reagent ion. See text for assignments of the observed ion peaks.

A second minor pathway to cyclohexanone involves decomposition of the 1-butyl-1-cyclohexoxy radical, predicted to be a minor pathway compared to isomerization ( $2.6 \times 10^4 \text{ s}^{-1}$  and  $2 \times 10^6 \text{ s}^{-1}$  at 298 K, respectively),



with the butyl radical forming butanal (~23%) and 4-hydroxybutanal (~77%) (Atkinson *et al.*, 1995a).

The 2-butyl-1-cyclohexoxy and 3-butyl-1-cyclohexoxy radicals may dominantly isomerize, depending on whether or not the conformation of the 6-membered transition state is favorable. Otherwise, as for the 4-butyl-1-cyclohexoxy radical, they will react with  $\text{O}_2$  and decompose, with the decomposition being expected to be important (Aschmann *et al.*, 1997) and with the resulting ring-opened radicals reacting to form carbonylnitrates of molecular weight 217, hydroxycarbonylnitrates 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  $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$  at 169 u, which is isobaric with the  $[\text{M}+\text{H}-\text{H}_2]^+$  of the molecular weight 170 hydroxycarbonyl(s), and that the observed 185 u ion peak (Figure 15) is the  $[\text{M}+\text{H}-\text{H}_2]^+$  of this hydroxydicarbonyl.

Our product yield data given in Table 8 (assuming that butanal and cyclohexanone are formed as co-products) account for 65% of the reaction products and pathways (and taking the uncertainties into account, with a range of ~40-110%).

## Summary and Conclusions

This project has been successful and the two proposed tasks were completed. Specifically, we have:

1. Re-measured the alkyl nitrate yields from *n*-hexane, *n*-heptane and *n*-octane and developed methods to identify and quantify carbonyl-nitrates and hydroxynitrates.
2. Measured the room temperature rate constants for the reactions of the OH radical with *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane (in the presence of NO) and identified and quantified the reaction products.

Our principal findings are:

- We find lower alkyl nitrate yields from the OH radical-initiated reactions of *n*-hexane, *n*-heptane and *n*-octane than previously reported by this laboratory some two decades ago. Our present alkyl nitrate formation yields, obtained with improved analysis methods, supercede our previous data.
- Using negative ion API-MS with the addition of NO<sub>2</sub> to the chamber reaction mixture post-reaction to form [NO<sub>2</sub>·M]<sup>-</sup> 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, enables semi-quantitative determination of the yields of hydroxycarbonyl and hydroxynitrate products.
- Although the uncertainties in the measured concentrations of hydroxycarbonyls and hydroxynitrates are estimated to be in the range of a factor of 2-3 (and probably increasing with increasing size of the alkane), our data show that hydroxycarbonyl formation from the C<sub>5</sub>-C<sub>8</sub> *n*-alkanes is very important, accounting for the majority of the reaction products. The measured hydroxynitrate formation yields from the C<sub>5</sub>-C<sub>8</sub> *n*-alkanes are consistently ~25% of the corresponding alkyl nitrate yields.
- Using a relative rate method, rate constants for reactions of the OH radical with *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane were measured to be (in units of 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) 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.
- From the *n*-decane reaction, the products identified and quantified were: 2-, 3-, 4- and 5-decyl nitrate, hydroxycarbonyls and hydroxynitrates. From the 3,4-diethylhexane reaction the products identified and quantified were: acetaldehyde, propanal, 3-pentanone, 3-pentyl nitrate, hydroxycarbonyls and hydroxynitrates. From the *n*-butylcyclohexane reaction, the products identified and quantified were: butanal, cyclohexanone, hydroxycarbonyls and hydroxynitrates.

- The products identified from the OH radical-initiated reactions of *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane in the presence of NO show that the detailed reactions subsequent to 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, while the alkoxy radicals formed from 3,4-diethylhexane also decomposed to a significant or dominant extent leading to volatile products.
- The measured ratios of the hydroxynitrate yields to the alkyl nitrate yields were significantly lower for the three C<sub>10</sub> alkanes (~10%) than for the C<sub>5</sub>-C<sub>8</sub> *n*-alkanes (~25%). For 3,4-diethylhexane this lower ratio may reflect the lower fraction of the initially-formed alkoxy radicals which undergo isomerization.
- The estimation method proposed by Aschmann and Atkinson (1999) appears to be useful in that its quantitative predictions concerning the products formed and their yields were in generally good agreement with our experimental observations.
- Our alkyl nitrate, hydroxyalkyl nitrate and hydroxycarbonyl formation yields given in Table 9, combined with the literature carbonyl yields arising from alkoxy radical decomposition and reaction with O<sub>2</sub>, account for ~95%, ~80%, ~70%, ~55%, ~45-50%, ~70% and ~65% of the products formed from the OH radical-initiated reactions of *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-decane, 3,4-diethylhexane and *n*-butylcyclohexane (in the presence of NO), respectively, with uncertainties of approximately a factor of 1.5 in each case. We can therefore now account for most of the reaction products formed from these alkanes, and hydroxycarbonyl formation accounts for a significant fraction of these products. Hydroxyalkyl nitrate formation accounts for a few percent of the overall reaction products, and is 10-25% of the corresponding alkyl nitrate yields.

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 analyse under atmospheric conditions. Finally, the experimental data obtained during this contract have already been implemented into Carter's most recent detailed chemical mechanism (Carter, 2000).

Table 9. Products of reactions of the OH radical with the alkanes studied in this work, in the presence of NO.

alkane	yield (%)			
	carbonyls	alkyl nitrates	hydroxycarbonyls	hydroxynitrates
<i>n</i> -pentane	47	10.5	36	2.6
<i>n</i> -hexane	10	14.1	53	4.6
<i>n</i> -heptane	≤1	17.8	46	4.7
<i>n</i> -octane	≤1	22.6	27	5.4
<i>n</i> -decane		22.6	22	2.4
3,4-diethylhexane	~40	18	11	1.7
<i>n</i> -butylcyclohexane	7	19	37	2.3

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## Glossary

API-MS	Atmospheric pressure ionization mass spectrometry
API-MS/MS	Atmospheric pressure ionization tandem mass spectrometry
CAD	Collision activated dissociation
GC-FID	Gas chromatography with flame ionization detection
GC-MS	Gas chromatography-mass spectrometry
MS/MS	Mass spectrometry/mass spectrometry
nm	Nanometer ( $10^{-9}$ m)
NO <sub>2</sub>	Nitrogen dioxide
NO	Nitric oxide
NO <sub>x</sub>	Oxides of nitrogen
NO <sub>3</sub> radical	Nitrate radical
O <sub>2</sub>	Molecular oxygen
O <sub>3</sub>	Ozone
OH	Hydroxyl radical
PFBOH	Pentafluorobenzylalcohol
"precursor ion"	In MS/MS, the ion formed in primary ionization that is selected for secondary fragmentation by CAD
"product ion"	In MS/MS, the ion produced from the "precursor ion" by CAD
R•	Alkyl radical
RO•	Alkoxy radical

ROO•

Alkyl peroxy radical