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ATMOSPHERIC IMPACTS OF VOC EMISSIONS: FORMATION YIELDS OF ORGANIC NITRATES IN REACTIONS OF ORGANIC PEROXY RADICALS WITH NO

Final Report

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FINAL REPORT TO THE COORDINATING RESEARCH COUNCIL

PROJECT A-107

Atmospheric Impacts of VOC Emissions: Formation yields of organic nitrates in reactions of organic peroxy radicals with NO

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Executive Summary

The formation of photochemical smog in cities requires the presence of both oxides of nitrogen (NOx), which are typically formed from combustion processes, and volatile organic compounds (VOC). Alkanes have long been recognized as a major component of urban air, but as a result of their low reactivity, they have not received as much attention in recent years as aromatics. Nevertheless, they have an important role to play in urban air chemistry. The oxidation of alkanes by OH leads to the formation of oxygenated VOCs (OVOCs), and organic nitrates, $RONO_2$. With increasing activities involving the extraction of oil and natural gas in the United States, alkane chemistry is taking on a renewed importance. Furthermore, as emissions of NO_x decrease as a result of tighter emissions controls, the alkyl nitrates are gaining in importance as radical sinks, relative to nitric acid, for example.

It has been known since the 1980s that the yields of organic nitrates increase with (1) the size of the alkane, (2) increasing pressure, and (3) decreasing temperature. Yet, these nitrate formation yields remain uncertain, even from fairly simple alkanes. In particular, it has been accepted that the yields of nitrates from secondary RO_2 are roughly twice those of primary and tertiary RO_2, although the results of two recent, limited studies cast doubt on this. We have undertaken a systematic study of nitrate yields from mid-size alkanes (5-8 carbon atoms, linear and branched). The experiments were conducted in a 47-L stainless steel reactor with in-situ detection by FTIR, and external sampling by GC-FID. We have measured nitrate yields from a number of linear and branched alkanes at room temperature, using authentic standards to characterize the GC retention times, and also the sensitivity where possible. In agreement with previous studies, the yield of nitrates increases with the number of carbon atoms in the parent alkane. However, in contrast to the older experiments, the yields of primary and tertiary nitrates (normalized for site of attack) are found to be similar to those of the secondary nitrates from the same molecule. A full analysis of the products also gives insight as to the relative sites of attack in a given molecule.

In the atmosphere, Structure Activity Relationships predict that attack at tertiary sites will be predominant for branched alkanes. Thus, the finding here that tertiary nitrate yields are larger than thought will decrease ozone formation rates, especially in regions with high concentrations of alkanes, such as large urban areas, or close to oil and gas extraction activities. The results also show that there is a weak temperature dependence on these yields, but probably not as large as found previously.

Introduction

Despite several decades of study, the role of alkanes in the chemistry of the atmosphere remains subject to considerable uncertainty. Although they are undoubtedly present in anthropogenically impacted areas, their effects have recently been somewhat neglected. This is partly a result of their low reactivity, which means that they often are not major contributors to local ozone production, when compared to more reactive gases such as alkenes and aromatics. In spite of this, and partly as a result of their reduced reactivity, alkanes can be present at elevated levels, and hence can contribute significantly to the local and regional air quality.

Sources of alkanes to the atmosphere are varied, but include short-chain alkanes related to oil and natural gas extraction, mid-sized (often branched) alkanes released from gasoline refining and usage, and long chain alkanes associated with diesel fuel. This work concerns the atmospheric chemistry of some mid-sized (5-8 carbon atoms), linear and branched alkanes.

Intermediate-sized alkanes are typically found at elevated levels in areas impacted by oil and natural gas extraction – for example, this was the case during the Front Range Air Pollution and Photochemistry Éxperiment (FRAPPÉ) field project which took place in Colorado in 2014 [Flocke et al., 2019]. Oxidation of these alkanes by OH leads to formation of oxygenated VOCs (OVOCs), and organic nitrates.

$OH + RH (+ O_2) \rightarrow H_2O + RO_2$

$RO_2 + NO \rightarrow RO + NO_2$ $(1-\alpha)$

$RO_2 + NO + M \rightarrow RONO_2 (+ M)$ α

$RO \rightarrow \rightarrow OVOC + HO_2$

$HO_2 + NO \rightarrow OH + NO_2$

$NO_2 + h\nu (+ O_2) \rightarrow NO + O_3$

The organic nitrates are of particular importance, as their formation yields and ultimate fate both play a role in determining the lifetime and distribution of NOx, and hence of ozone production on a regional scale [Flocke et al., 1995; Perring et al., 2010]. Higher nitrate yields imply less available NO_x, and consequently a lower local ozone production rate. Conversely, the nitrates, which are relatively long lived, can be transported over long distances before reacting to release the NO_2, which can then contribute to remote ozone formation. In classical, urban scenarios, the main loss rate for NO_x in the atmosphere is through the reaction of OH with NO_2, forming nitric acid. However, in recent years, NO_x levels over the continental U.S. have dropped considerably as a result of improved emission controls and cleaner engines [Russell et al., 2012]. Consequently, it has been proposed that over a large area of the U.S. the formation of alkyl nitrates is becoming the limiting factor in determining the lifetime of NO_x [Li et al., 2018]. Thus, it becomes imperative to conduct experiments to better define the yields of these nitrates as a function of the size and structure of the alkane.

It has been known for many years that the yields of organic nitrates increase with the size of the alkane, with increasing pressure, and with decreasing temperature [Atkinson et al. 1982b, 1984b, 1987, 1995; Arey et al., 2001; Aschmann et al., 2001]. Yet, these nitrate formation yields remain uncertain, even from fairly simple alkanes. In general, it is thought that the yields of nitrates from secondary RO_2 are roughly twice those of primary and tertiary alkanes, on the basis of data from Atkinson's group, published in the mid to late 1980s. However, Espada et al. [2005] provided evidence that the site-specific yields of 1-butyl nitrate and 2-butyl nitrate were equal. Cassanelli et al. [2007] showed that the yields of the nitrates from isopentane, a major component of gasoline emissions, are largely independent of the structure of the radical. We also obtained preliminary results indicating that the yields of tertiary nitrates, the major nitrates formed from branched alkanes, are severely underestimated. We believe that this is due to the fact that these nitrates are thermally unstable, and hence tend to decompose in the heated inlet of the gas chromatographs used to quantify them. To add to the uncertainty, the Riverside group (Atkinson and coworkers) later revised their earlier alkyl nitrate yields [Arey et al., 2001], but many models, e.g., the Master Chemical Mechanism, version 3.3.1 [Saunders et al., 2003], still use the old, uncorrected data. Hence, it seems timely and appropriate to undertake a careful, systematic study of the formation yields of some targeted alkyl nitrates in order to assess the state of knowledge. These uncertainties in our knowledge of alkyl nitrate yields hinder the accurate assessment of the atmospheric impact of the overall alkane oxidation cascade on NOx lifetime and distribution, with a concomitant lack of ability to accurately predict ozone production.

Project Objectives:

The main goal of the work is to be able to better determine the overall impact on air quality of some five- to eight-carbon alkanes and their atmospheric by-products, particularly in areas impacted by oil/natural gas extraction.

The objectives are to obtain yields of organic nitrates from oxidation of the alkanes, as a function of the structure and size of the alkane, and also as a function of temperature. This collective dataset will be made available for incorporation into process- and regional-scale models (including those in use at NCAR), so that more accurate predictions can be made of ozone production on urban/regional scales, and areas impacted by oil and natural gas extraction.

Experimental

The experiments were conducted in a 47-L stainless steel reaction chamber fitted with Al-coated mirrors for infrared analysis of the contents [Shetter et al., 1987]. The chamber could be cooled to 250 K using a circulating bath with ethanol as the coolant. Experiments were conducted at room temperature (296±2) K, at (270±2) K and at (250±2) K. Gases were added to the chamber using a glass vacuum line and standard manometric techniques. Samples were added to the chamber by introducing a known pressure of the target gas into a 1-L glass bulb on the vacuum line, and sweeping the sample into the chamber using dry N_2 gas from a liquid nitrogen dewar. Multiple, consecutive additions could be made this way.

Hydroxyl radicals were produced by the photolysis of isopropyl nitrite in the presence of NO. The UV radiation for photolysis was provided by a 200-W Xe-arc lamp ($\lambda > 300$ nm) fitted with a black-glass filter that was held in a water-cooled housing to eliminate unwanted IR wavelengths and to cool the filter.

$i\text{-}C_3H_7ONO + h\nu \rightarrow i\text{-}C_3H_7O + NO$

$i\text{-}C_3H_7O + O_2 \rightarrow CH_3C(O)CH_3 + HO_2$

$HO_2 + NO \rightarrow OH + NO_2$

$OH + \text{alkane} \rightarrow \text{products}$

Infrared spectra of the starting materials and products were measured using a Bomem DA-8 spectrometer with a liquid nitrogen cooled Hg-Cd-Te detector. Between 40 and 400 scans were averaged to improve the signal to noise. Authentic standards were used whenever possible to calibrate the spectra. Concentrations were obtained by spectral subtraction (stripping) of the spectrum of a pure standard. Alkyl nitrates were quantified using integrated infrared band strengths of 3.0×10^{-17} cm^2 molecule^{-1} for bands near 1280 cm^{-1} (symmetric stretch), and 5.4×10^{-17} cm^2 molecule^{-1} near 1650 cm^{-1} (asymmetric stretch). These band strengths are in good agreement with those reported by Tuazon and Atkinson [1990], and confirmed by measurements of our commercially available standards.

Concentrations in the chamber were also measured using an Agilent 6890N gas chromatograph with flame ionization detection [McGillen et al., 2016]. Gas was flowed from the chamber through a 1/8" o.d. tube to a 6-port valve. Samples were collected in a 25 cm long loop of 2-mm o.d. PEEK tubing connected to the 6-port valve, before injection into the GC. The sample loop was kept at ambient temperature, and provided enough signal for adequate quantification of the samples without the need for cryotrapping. The GC temperature profile was 3 minutes at

28 ^oC, followed by a ramp of 20 ^oC min^{-1} for 7.1 minutes, to bring the temperature to 170 ^oC, followed by 1 minute at 170 ^oC. This enabled alkyl nitrates up to ~C8 to be quantified.

Experimental Protocol

The typical experimental protocol was as follows. Oxygen was first added to the chamber at a pressure between 150 and 450 Torr (usually 300). Isopropyl nitrite (4-7) x 10^{14} molecule cm^{-3}, alkane (2.1-4.2) x 10^{14} molecule cm^{-3} and NO (1.4-4.3) x 10^{14} molecule cm^{-3} were then swept into the chamber individually from the 1-L bulb using N_2 carrier gas from liquid nitrogen boil-off. The pressure was brought to ~720 Torr, and the mixture allowed to stabilize before recording an infrared spectrum of the starting mixture (400 scans). Then, a Teflon valve on the outlet of the chamber was opened, and approx. 200 cm^3 of the mixture (corresponding to a chamber pressure drop of ~ 3 Torr) was flowed through the GC sample loop (since atmospheric pressure is ~630 Torr in our laboratory). The flow was then stopped and the gas in the loop was allowed to stabilize for up to a minute, to ensure that it was at ambient pressure. Then the gas was injected into the GC with He carrier gas via the 6-port valve. Three short chromatograms were taken with the oven held at 28 ^oC (which covered the retention times of the nitrite and the alkanes) followed by one chromatogram using the full temperature profile. During the fourth chromatogram the gas mixture in the chamber was exposed to UV light by lifting a shutter, and the mixture was allowed to react for 20-50 minutes. IR spectra were taken periodically (using 40 scans) while the chamber was being irradiated, to make sure that the NO had not completely reacted away. When the NO had reached 10-15% of its starting amount, the shutter was closed to end photolysis. Nitrogen was then added to the chamber, along with additional NO (2.1 x 10^{14} molecule cm^{-3}), up to a pressure of ~760 Torr, to mix the contents. After a few minutes, an IR spectrum was taken, and the mixture was again sampled into the GC loop. Two full chromatograms were taken, in order to quantify the nitrates (retention times 5-8 minutes, depending on size). Following the injection of the second GC sample, irradiation continued for another 20-30 minutes, after which the pressure was increased to ~820 Torr with N_2, and IR spectra and GC samples were again taken. The addition of the extra N_2 ensured that the contents of the chamber were well-mixed, so that the GC sampled a representative sample of gas. The initial concentration of NO was kept as low as possible, to minimize the formation of alkyl nitrates from the secondary reaction of alkoxy radicals with NO_2.

$RO + NO_2 + M \rightarrow RONO_2 + M$

Addition of extra NO after the first irradiation ensured that all peroxy nitrates, which are thermally unstable, were removed from the system.

$RO_2 + NO_2 \leftrightarrow RO_2NO_2$

$RO_2 + NO \rightarrow RO + NO_2$

Authentic samples of the alkanes, their expected carbonyl products and alkyl nitrates were introduced into the chamber via the 1-L bulb, with N_2 carrier gas up to a pressure of 760 Torr, and these were used to calibrate the IR spectra and the GC response. The GC response was found to vary linearly with the number of carbon atoms in the alkanes, N_C, with an average sensitivity of 2.5×10^{-14} (C-atom)$^{-1}$. The carbonyls and nitrates were found to have a reduced response (proportional to N_C-1 for the carbonyls and roughly N_C-0.5 for the nitrates). Figure 1 shows the GC response for a number of nitrates plotted against the integrated area of the IR band centered near 1650 cm^{-1}. The intensity of this band is assumed to be independent of the molecule for most nitrates. Hence, the slopes show the relative GC response for C3, C4 and C5 nitrates. The C3 and C4 species were commercial samples, and so absolute calibrations were feasible by introducing a known concentration to the chamber using the 1 L bulb. The C5 nitrates were synthesized in-house and showed some impurities, and so the IR was used to determine the concentration in the chamber. The slopes of the plots are 0.30, 0.48, and 0.70. Using an infrared band strength of 5.4×10^{-17} cm molecule^{-1} leads to sensitivities for the nitrates of 5.3, 8.4 and 12.2×10^{-14} molecule^{-1} for the C3, C4 and C5 nitrates. It can also be seen that the data points for 2-pentyl and 3-pentyl nitrate fall on the same line, showing that the sensitivity is independent of the isomer, as expected. Using a sensitivity of 2.5×10^{-14} (C-atom)$^{-1}$ derived from the alkanes, gives an equivalent carbon number of 2.1, 3.4 and 4.9 for the C3, C4 and C5 nitrates, respectively.

For samples taken at a chamber pressure of P_C and a temperature of T_C the gas concentrations measured in the sample loop were corrected by a factor $(P_C/760)\mathrm{x}(296/T_C)$ to allow for the fact that the GC response for the same number density of sample gas in the chamber varies with the pressure and temperature in the chamber (since the pressure in the sample loop is always ambient, the GC is essentially measuring mixing ratio, not concentration). As noted earlier, standard responses were measured at 760 Torr, so experimental samples were corrected to this pressure.

Sample Preparation

Commercially available liquid samples were prepared by freeze-pump-thaw cycles. Authentic standards of the alkanes and several reaction products were added to small glass vials fitted with stopcocks, which were then attached to the vacuum line. The samples were frozen and evacuated several times to remove air and volatile impurities, before adding headspace vapors from these purified samples to the chamber via the 1-L glass bulb on the vacuum line. Isopropyl nitrite was prepared by dripping 50% H_2SO_4 into a stirred suspension of sodium nitrite in isopropyl alcohol in an ice bath. A slow flow of N_2 carried the nitrite through a bubbler filled with saturated NaOH solution (to remove HONO) and a column of $CaCl_2$ (to remove H_2O) and into a sample vial cooled to -80 ^{0}C. After all the acid had been added, a few mL of the isopropyl nitrite (pale yellow liquid) was present in the collection vial. The vial was then transferred to the vacuum line, the sample frozen and evacuated to remove air and NO. IR spectra of the sample occasionally revealed the presence of N_2O (especially if the reaction flask was allowed to get too warm); N_2O could easily be removed by pumping for a short while at -80 ^oC without losing the nitrite sample.

Alkyl nitrate samples were prepared by 2 different methods, the principles of which are summarized in Boschan et al. [1955]. The first involved slowly dripping a mixture of H_2SO_4-HNO_3 into the corresponding alcohol, which was being stirred vigorously at -5 ^oC (obtained by adding rock salt to ice). A small amount of urea was added to the alcohol to reduce the formation of nitrous acid, HONO. Extreme care was taken to ensure that the temperature did not increase above about 2-3 ^oC, and that NO_2 was not visible in the headspace. After addition of the acid, a yellow, oily layer could be observed at the surface. The reaction mixture was then transferred to a pear-shaped separating funnel, water was added and the mixture shaken to cause the oily nitrate layer to separate from the acid layer. The aqueous layer was then run off, and the organic layer collected and dried with $CaCl_2$. This method of preparation worked with secondary nitrates, for which the rate of hydrolysis is relatively slow. Variations were tried where the acid was added to the alcohol or vice versa, or using suspended sodium nitrate in place of the nitric acid, but the method described worked the best. For tertiary nitrates GC samples of the reaction headspace indicated that the nitrates were being formed, but their rapid hydrolysis prevented them from being separated successfully at the end of the reaction.

A second method, which worked for all nitrates, was to dissolve 10 g $AgNO_3$ in 50 mL acetonitrile, and then add this to 4 mL alkyl bromide. The mixture was stirred in a round bottom flask at room temperature. A milky yellow suspension of AgBr began to appear after a few minutes. The composition of the headspace was monitored by GC, and the reaction was allowed to proceed until all the alkyl bromide had reacted away (typically, the $AgNO_3$ was not quite enough, so a little more was added to just remove the alkyl bromide). Then the AgBr was filtered out using filter paper, and the liquid was transferred to a rotary evaporator to remove the excess acetonitrile under vacuum. After further filtration to remove $AgNO_3$ that had precipitated out, the sample was transferred to a glass vial, and the remaining acetonitrile removed by pumping on the vacuum line at reduced temperature. This method proved viable for the preparation of primary, secondary and tertiary nitrates.

Six nitrates were separated and purified in this way, and in addition, commercial samples were obtained for isopropyl, 1-butyl, and isobutyl nitrates. Gas samples extracted from the headspace of the reaction mixtures allowed monitoring of the extent of reaction and also identification of the retention time of the specific nitrate being produced.

Analysis of Experimental Data

Typical experiments consisted of the photolysis of isopropyl nitrite in the presence of NO and an alkane for two irradiation periods. For some experiments, two alkanes were added, to obtain relative product yields. Following the irradiation periods, the IR spectra were analyzed for alkane, nitrite, NO, NO_2, HCHO, acetone, and total nitrates (using the integrated band strength for the bands near 1280 or 1660 cm^{-1}). The gas chromatograms provided concentrations of the alkane, primary carbonyl compounds, and speciated alkyl nitrates. Reaction of OH radicals with an alkane gives a number of RO_2 radicals (depending on the number of sites of attack available on the alkane, and their relative reactivity). These various RO_2 radicals react with NO to form alkoxy radicals or alkyl nitrates. For the larger, branched alkanes the alkoxy radicals decompose to give a carbonyl and a smaller alkyl peroxy radical, which can itself react with NO to give an alkyl nitrate. Thus, the distribution of alkyl nitrates can give information not only on the primary nitrate yields, but also on the decomposition tendencies of the alkoxy radicals.

$OH + RH (+ O_2) \rightarrow H_2O + RO_2$

$RO_2 + NO \rightarrow RO + NO_2$

$RO_2 + NO + M \rightarrow RONO_2 + M$

$RO + O_2 \rightarrow \text{carbonyl1} + HO_2$

$RO (+ O_2) \rightarrow R'O_2 + \text{carbonyl2}$

$R'O_2 + NO \rightarrow R'O + NO_2$

$R'O_2 + NO + M \rightarrow R'ONO_2 + M$

$HO_2 + NO \rightarrow OH + NO_2$

In this simplified scheme, the alkyl fragment R’ is smaller than the initial alkyl group R.

Conditions for the various experiments are summarized in Table 1, which lists the temperature and pressure, and initial reactant concentrations for each experiment. In order to obtain nitrate yields from the experiments, the relative importance of each site of attack must be known. In general, these are not known from experiments, but must be calculated using structure activity relationships (SAR). The SARs for atmospheric OH reactions with alkanes were introduced by Atkinson and coworkers in the 1980s [Atkinson et al., 1982a, 1984a], were updated by Kwok and Atkinson [1995], and have been recently revised in a more global manner by Jenkin et al. [2018]. Measurements of rate coefficients and mechanisms for the reactions of OH with alkanes have been evaluated by Calvert et al. [2008]. SARs are a way to estimate the overall rate coefficient for an abstraction reaction, by considering the influence of neighboring groups on the rate of reaction at a given carbon atom. The overall rate coefficient is obtained by summing the individual contributions. The fractional extent of reaction at any given carbon atom is then assumed to be given by its partial rate, divided by the total rate. This is the approach used here to obtain the fractional site of attack. While SARs do not work very well for predicting the overall rate coefficient for OH with multiply-oxygenated molecules, they do appear to work very well in predicting the overall rate coefficient for alkanes [Jenkin, 2018] (but see later for a discussion of multiply-branched alkanes). Hence the assumption is made that the representation of the fractional sites of attack is also reasonable, and that the SAR can be used to estimate the distribution of RO_2 from a given alkane reacting with OH. In general, the SAR predicts the dominant site of reaction with OH to be at tertiary carbon atoms.

Once the relative rates of formation of the various RO_2 have been calculated, the identities of the various nitrates must be assessed. In general, secondary nitrates elute before tertiary, which elute before primary, for a given parent molecule. As noted earlier, we attempted to synthesize many of the nitrates encountered in this study. Even if it was not always possible to purify a specific nitrate, a positive identification could always be made by sampling the headspace of the reaction flask, in order to obtain the appropriate retention time.

Reactions were also conducted using chlorine atoms to initiate the reaction rather than OH. In the initial stages this was useful for identifying the retention times of the nitrates. However, the use of chlorine has the drawback that the HO_2 radicals produced react with NO to form OH, so the chemical system is not clean. The exception is cyclohexane, where only one site of attack is available. The use of chlorine was, however, beneficial in that the distribution of alkyl peroxy radicals is different from that produced by OH (Cl typically giving less tertiary, more primary and secondary alkyl peroxy radicals than OH) thus providing an additional confirmation of the identity of the GC peaks. The results of Cl-atom experiments have thus been included where they were of value.

Results

Relative nitrate yields

As found by Atkinson and coworkers [Arey et al., 2001; Atkinson, R., Pers. Comm., 2018], and confirmed here, the GC-FID sensitivity for a set of nitrate isomers of given carbon number is the same. Hence, a comparison of the GC peak areas should correspond to the relative concentrations of the nitrates. Thus, the simplest analysis involved finding the total nitrate peak area, using this to calculate the relative distribution of nitrates, and comparing that to the fractional distribution of RO_2 given by the SAR. A sample chromatogram is shown in Figure 2, using 2-methyl pentane as an example. The SAR predicts a distribution sec(1):sec(2):tert:prim(1):prim(2) of 21:28:40:7.0:3.5 while the relative nitrate peaks (averaged over three independent chromatograms) are 20:28:42:6.5:3.5 (see following section for a more specific identification of the peaks). It can be seen immediately that within the assumptions of similar sensitivity for the different nitrate isomers, and accuracy of the SAR in representing the relative RO_2 distribution, the yields of primary, secondary and tertiary nitrates are essentially equal, on a per RO_2 basis. This conclusion is independent of any knowledge of the absolute concentrations of the alkane or nitrates. Similar conclusions were found for isopentane and 3-methyl pentane (see later) which also produce a mix of all three types of nitrate.

A few experiments were also conducted using a mixture of two alkanes to obtain relative nitrate yields. In this case it was necessary to know the overall rate coefficient of each alkane with OH, to ascertain the relative extent of conversion of each. The initial concentrations of the alkanes were selected to be inversely proportional to their rate coefficients, so that the amount of each alkane converted should be approximately the same. Initial experiments of this sort used pentane in addition to one alkane, since the secondary nitrate yields from pentane are well established [Atkinson et al., 1995; Arey et al., 2001]. However, the GC elution time of pentane is very similar to those of both isopropyl nitrite and acetone (produced from isopropyl nitrite photolysis). So, later measurements were made relative to isopentane, which has a well separated GC peak.

Individual Alkanes

Pentane

The distribution of nitrates from pentane has been studied extensively by Atkinson et al. [1995], who showed that the ratio of the 2-nitrates and 3-nitrates was in agreement with SAR predictions of the site of attack. They also found the (site-specific) secondary nitrate yields to be (11.5±1.3)%. We observed the formation of three nitrates, as expected, eluting in the order 3-pentyl, 2-pentyl and 1-pentyl nitrate, see lower trace of Figure 3. The loss of pentane was measured by IR, since, as mentioned above, the retention time of pentane is similar to those of isopropyl nitrite and acetone. Based on the loss of pentane, the yields of the nitrates were 0.047, 0.065, and 0.0105, respectively. Normalizing by the site of attack (0.366:0.542:0.092) gives site-specific yields of 0.127, 0.121, and 0.113, for the 3-, 2-, and 1-pentyl nitrates. The overall yield of nitrates was 0.120. Since the 3- and 2-nitrates are both secondary, no difference in yield is expected. However, the comparable yield for the 1-pentyl nitrate is counter to the yields measured by Atkinson et al. in the 1980s, where much lower yields of primary nitrates were found. It should be noted that the overall yields of primary nitrates are small (and hence difficult to measure) and the branching ratios for attack at the primary sites are the smallest and least certain.

Yields of the carbonyls 3-pentanone and 2-pentanone were found to be 0.155 and 0.044, respectively. While the fraction of attack is higher at the 2-site (as reflected in the nitrate yield) the 2-pentoxy radical is able to isomerize rapidly, leading to a lower yield of the ketone.

One experiment was conducted at a temperature of 270 K. The nitrate yields were found to be 0.051, 0.072, and 0.009. Normalizing by the site of attack predicted by the temperature dependent SAR of Jenkin et al. [2018] leads to site specific nitrate yields of 0.137, 0.130, and 0.129, and an overall nitrate yield of 0.132. The results are indicative of a small temperature dependence, but not as large as that found by Atkinson and coworkers in their early work, who found an increase of roughly 40% in going from room temperature to 273 K. Additional experiments conducted at 250 K are still under analysis, but indicate that production of alkyl nitrates from the RO + NO_2 reaction was occurring, which needs to be correctly accounted for before any conclusions can be drawn.

Cyclohexane

The nitrate yields from cyclohexane have been measured several times. Cyclohexane provides an interesting case, since it consists of identical $–CH_2–$ groups, and thus only one nitrate is formed, which is secondary in nature. Thus, it does not matter whether OH or Cl is used to initiate the reaction, and both were used here. The main products observed were (in order of retention times) cyclohexyl nitrite, cyclohexanone, and cyclohexyl nitrate, whose retention time was confirmed via synthesis of an authentic sample using the reaction of cyclohexyl bromide with $AgNO_3$.

From 2 experiments, each consisting of 2 irradiations, cyclohexyl nitrate yields of 0.186 were obtained. A single experiment was conducted using both cyclohexane and pentane. Figure 3 shows a chromatogram from a cyclohexane experiment (upper trace), along with a mixed pentane-cyclohexane experiment (middle trace). Their OH rate coefficients are in the ratio 1.71 (=6.78/3.96, each in units of 10^{-12} cm^3 $molecule^{-1}$ s^{-1}) [Calvert et al. 2008], so a pentane/cyclohexane ratio of 1.67 was used. As can be seen, the peak from cyclohexyl nitrite, visible in the cyclohexane experiment at 5.15’, partially overlaps the peak from 3-pentyl nitrate at 5.18’ in the mixed experiment. However, the peaks can be quantified reliably. The yield of cyclohexyl nitrate relative to the sum of pentyl nitrates was a factor of 1.34 higher. Taking the average pentyl nitrate yield measured above as 0.12, gives a yield of cyclohexyl nitrate of 0.16. This is a little lower than the individual measurements but clearly consistent with those values. Literature values for the yield of cyclohexyl nitrate near 298 K range from 0.09±0.05 to

0.17±0.04, with a consensus value around 0.16 [Aschmann et al., 1997; Platz et al., 1999; Orlando et al., 2000; Espada et al., 2005].

Two experiments were conducted at 270 K, using OH as the reactant. Nitrate yields of 0.25±0.03 were measured, which is slightly larger than measured by Orlando et al. [2000] using infrared absorption. Further experiments were conducted at 250 K; 2 using Cl-atoms and one OH. Six chromatograms were obtained. Although the results were more scattered than at the two higher temperatures, a further increase in nitrate yield was found, 0.31±0.04. Analysis of these experiments is continuing, to determine the extent of formation of cyclohexyl nitrate via RO + NO_2.

Isopentane

Isopentane (2-methyl butane) is the simplest molecule to contain primary, secondary and tertiary carbon atoms, and so is a good test case for comparing yields of the different types of nitrate. Oxidation of isopentane with both Cl atoms and OH radicals did indeed show all three types of nitrate, with their retention times confirmed by synthesis. The two primary nitrates were overlapped in the GC, but their peaks were clearly in a ratio 2:1; consequently, the sum was taken, and divided in the expected ratio.

At 296 K, with OH as reactant, the yields of secondary, tertiary and primary nitrates were 0.033, 0.085 and 0.014, respectively. Normalizing for the fractional attack by OH of 0.29, 0.56 and (0.10+0.05) gives site specific nitrate yields of 0.11, 0.15 and 0.10. This is in contrast to previously measured secondary and tertiary nitrate yields of 0.15 and 0.056 [Atkinson et al., 1987]. Furthermore, the current version of the Master Chemical Mechanism uses yields (sec, tert, prim) of 0.14, 0.047 and 0.052. Clearly, in spite of some variations, there is no evidence from our results of primary and tertiary nitrate yields being substantially lower than secondary.

At 270 K, the yield of tertiary nitrate is expected to increase, while those of secondary and primary nitrates should decrease, as a result of the lower activation energy for abstraction at the tertiary site. The yields of secondary, tertiary and primary nitrates were 0.032, 0.097, and 0.0137. Normalizing the measured yields for the temperature-corrected site of attack yields site specific nitrate yields of 0.12, 0.16, and 0.11. Again, the yield of the tertiary nitrate is larger than those of secondary and primary. This may be a real effect, or may reflect a deficiency in the SAR in predicting the sites of attack. Production of nitrates by reaction of RO with NO_2 was not thought to be an issue in these experiments, since low concentrations of NO_x were used (~10 ppm) with low conversion of NO to NO_2. Furthermore, the 3-methyl-2-butoxy and 2-methyl-2-butoxy radicals both decompose relatively rapidly, even at lower temperatures. The change in yield with temperature is, as in the case of pentane, much less than found by

Atkinson et al. [1987], but similar to the change measured by Cassanelli [2007] over the same temperature range (increasing from 0.11 to 0.14 for the tertiary nitrate).

3-Methyl pentane

3-Methyl pentane, like isopentane, contains one unique secondary site, one tertiary, and two primary. However, upon oxidation, 5 nitrate peaks were observed in the GC. Two of the peaks are from diastereomeric isomers [Atkinson et al., 1987] of the secondary nitrate (non-superimposable isomers containing two asymmetric carbon atoms), which are separated in the GC (see Figure 4). An authentic sample of 3-methyl-2-pentyl nitrate was made by nitrating the alcohol, 3-methyl-2-pentanol. Both the alcohol and the nitrate showed double peaks of roughly similar magnitude in the GC, confirming the identity of the peaks as diastereomers that are separable on the GC column. The primary nitrate peaks were in this case well separated in the chromatogram. Combining the areas of both the secondary nitrate peaks then gave yields of secondary 0.068, tertiary 0.095, primary (1) 0.011, primary (2) 0.005. Normalizing by the sites of attack (0.39:0.51:0.066:0.033) yields 0.17, 0.18, 0.17 and 0.15 for the yields of secondary, tertiary and the two primary nitrates. Clearly, these yields are essentially indistinguishable for the three types of nitrate, within the expected uncertainties of around ±0.03. Atkinson et al. [1984, 1987] found yields of 0.16 and 0.18 for the secondary nitrate at 298 K and 760 Torr. However, much smaller yields for the tertiary and primary nitrates would have been previously assumed, in contrast to our data.

Similarly, at 270 K, yields of 0.18±0.02 were found for each of the nitrates. As in the study of pentane, these value do not show the large increase with temperature (~30%) found for the secondary nitrates in previous work [Atkinson et al., 1987].

2-Methyl pentane

As shown earlier, the oxidation of 2-methyl pentane, leads, as expected to two secondary nitrates, one tertiary, and two primary. At 296 K, the site-specific nitrate yields were: secondary (1) 4-methyl-2-nitrooxy pentane, 0.181; secondary (2) 2-methyl-3-nitrooxy pentane, 0.195; tertiary 2-methyl-2-nitrooxy pentane, 0.192; primary (1) 2-methyl-1-nitrooxy pentane, 0.176; primary (2) 4-methyl-1-nitrooxy pentane, 0.175. Again, these data show little or no variation in yield, and are similar to those derived for cyclohexane and 3-methyl pentane (which have the same number of carbon atoms). One experiment was carried out using a mixture of pentane and 2-methyl pentane. The sum of nitrates from 2-methyl pentane was 1.30x those from pentane. Using a combined yield of 0.12 for pentane, leads to a nitrate yield of 0.16 for 2-

methyl pentane, which is slightly smaller than the individually measured values, but well within the combined uncertainties. According to the parameterization of Arey et al. [2001], the nitrate yield for C5 and C6 alkanes should be 11.8% and 15.6%, very consistent with our relative yields measured for both 2-methyl pentane and cyclohexane.

Larger alkanes

A few experiments were carried out using 2,4-dimethyl pentane and 2,2,4-trimethyl pentane. The gas chromatograms for these molecules contained numerous peaks in the region where nitrates are expected, but by using both Cl atoms and OH radicals, a consistent set of peaks could be identified as nitrates. Interestingly, for these experiments, the tertiary nitrate yields were somewhat lower than expected based on the SARs. For example, in the case of 2,4-dimethyl pentane, which only contains one unique primary site, one secondary and one tertiary, the tertiary nitrate yield was 0.53 (relative to the sum of nitrates), whereas the SAR predicts a fractional attack at that carbon atom of 0.66. The measured value is thus considerably less than expected.

Some insight can be gained by comparing the measured rate coefficients for OH reaction with these molecules with those predicted by the SAR. In the case of 2,4-dimethyl pentane, the published rate coefficients are not in particularly good agreement, with values ranging from 4.8×10^{-12} (Atkinson et al., 1984a) to 6.3×10^{-12} cm^3 $molecule^{-1}$ s^{-1} (Wilson et al., 2006). We have measured the rate coefficient for 2,4-dimethyl pentane relative to those of isopentane and ethene. Figure 5 shows plots of $\ln([2,4DMP]_0/[2,4DMP]_t)$ versus the corresponding quantity for isopentane (upper plot) and ethene (lower plot). The slopes are 1.25 ± 0.05 and 0.58 ± 0.06, respectively. Using recommended rate coefficients for the reference reactions of 3.6×10^{-12} and 7.8×10^{-12} cm^3 $molecule^{-1}$ s^{-1} leads to values of (4.5 ± 0.3) and $(4.5\pm0.5)\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} relative to the two reference compounds, in good agreement with Atkinson's value.

For 2,4-dimethyl pentane, the SAR predicts a rate coefficient of $\sim6\times10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, whereas the measured rate coefficient is only 4.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. This suggests that the SAR is not doing a very good job at predicting the site of attack for larger, branched alkanes, and that the fraction of reaction at the tertiary sites is being overestimated. This could be a result of steric effects at these tertiary sites, as has been suggested previously for 2,2,4-trimethyl pentane and 3,4-diethyl hexane [Aschmann et al., 2001, 2002]. Taking our measured nitrate yields as representing the site of attack, and using our overall measured rate coefficient of 4.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1} leads to a partial rate coefficient for reaction at the secondary –CH_2– group of 1.37×10^{-12} cm^3 $molecule^{-1}$ s^{-1}, which is identical to that predicted by the SAR, 1.40×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. This is thus a further indication that reaction at the tertiary site is hindered in some way, while reaction at the secondary (and presumably primary) sites is “normal”.

A similar situation occurs in the case of 2,2,4-trimethyl pentane (aka isooctane). The rate coefficient has only been measured twice. The room temperature values are in reasonably good agreement, and a recommended value is 3.3×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. However, the SAR value is 30% higher than this, 4.5×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. As a result of the number of peaks appearing in the GC, it was difficult to identify the individual nitrates. However, a careful examination of the retention times of experiments using both Cl atoms and OH allowed a reasonable identification of nitrate peaks from 2,2,4-trimethyl pentane. According to the SAR, the tertiary nitrate should dominate the OH experiments, and should be twice as large in the OH experiments as in the Cl experiments. However, all the peaks were similar in both experiments. We varied the heating rate for the GC oven to allow the peaks to elute as low as 60° C, but no change in the relative distribution was found, inferring that we were not losing the tertiary nitrate in the column. This suggests (although does not prove) that the extent of reaction at the tertiary site is less than expected from the SAR. Aschmann et al. [2001, 2002] studied the oxidation of 2,2,4-trimethyl pentane and 3,4-diethyl hexane, and found that the OH rate coefficients are 30-40% lower than expected, and that the total product yields do not agree with the predicted site of attack. However, our measurements, which accounted for all the nitrates formed, give a much more direct indication that the tertiary sites are less reactive than expected, possibly due to steric hindrance [Aschmann et al., 2001, 2002].

Conclusions

We have measured organic nitrate yields for a series of alkanes, linear and branched, at room temperature and below. In contrast to earlier work, we find that the yields of primary and tertiary nitrates are similar to those of secondary nitrates for molecules with the same carbon number. The most convincing evidence comes from a consideration of the relative yields of nitrates produced from the branched alkanes, which contain a mixture of all three types, so the reactions are essentially internally calibrated. The uncertainty on a given nitrate yield is 10-15% of the quoted value, as a result of the low nitrate signals and the difficulties in measuring the absolute change in the alkane. However, the internally consistent ratios of nitrates are much more precise, and show clearly that the nitrate yields are indistinguishable, within the limitations of the SAR used to determine the OH site of reaction.

The work of Atkinson’s group, carried out in the 1980s, suggested that yields of primary and tertiary nitrates are about a factor of 2-3 lower than those of secondary nitrates, and this is the basis for most current models, including the Master Chemical Mechanism. The reasons for the discrepancies are not clear, but in the case of tertiary nitrates could be a result of hydrolysis of the nitrates in the cryotraps used, or thermal decomposition in the GC inlet. We have been very careful to collect samples in a continuously flushed loop at room temperature, and to inject and elute them at relatively low temperatures, thus minimizing the potential for losses. The low yields of primary nitrates in the earlier work remain unexplained, but may simply reflect the low absolute yields, and the difficulty in measuring them on older, wide-bore, packed columns.

In the atmosphere, SAR relationships predict that attack at tertiary sites will be predominant for branched alkanes. Thus, the finding here that tertiary nitrate yields are larger than thought will decrease ozone formation rates, especially in regions with high concentrations of alkanes, such as large urban areas, or close to oil and gas extraction activities. The results also show that there is a weak temperature dependence on these yields, but probably not as large as found previously. While the formation of nitrates due to reaction of RO with NO_2 cannot be ruled out in some of the colder experiments, that reaction would only lead to overestimate of the yields. Further analysis of these experiments, down to 250 K, is still in progress. Also, the nitrate yields have not been corrected for loss by reaction with OH. However, since the alkane conversions were kept low (20% or less), OH reaction would lead to an underestimation of the yields by 10% at most (see Bedjanian et al. [2018], and references therein, for rate coefficients for OH + alkyl nitrates).

The reaction of organic peroxy radicals to form organic nitrates is thought to proceed through an unstable peroxynitrite intermediate, $ROO + NO \rightarrow [ROONO]^* \rightarrow RONO_2$. Although the reaction seems simple on paper, a complete theoretical description of the reaction has proven to be curiously intractable to date [Barker et al., 2003; Zhang et al., 2004; Butkovskaya et al., 2015; Piletic et al., 2017]. Any model of the reaction has to be able to predict the competition with the major reaction pathway (to give alkoxy + NO_2), the pressure and temperature dependence of the yield, any dependence on the size of the alkyl group and location of the peroxy group (although we have shown this to be less important than previously thought), and the currently disputed effect of functional groups within the molecule (hydroxyl, carbonyl, nitrate, etc). Clearly, such advances can only come as a result of further detailed experimental work.

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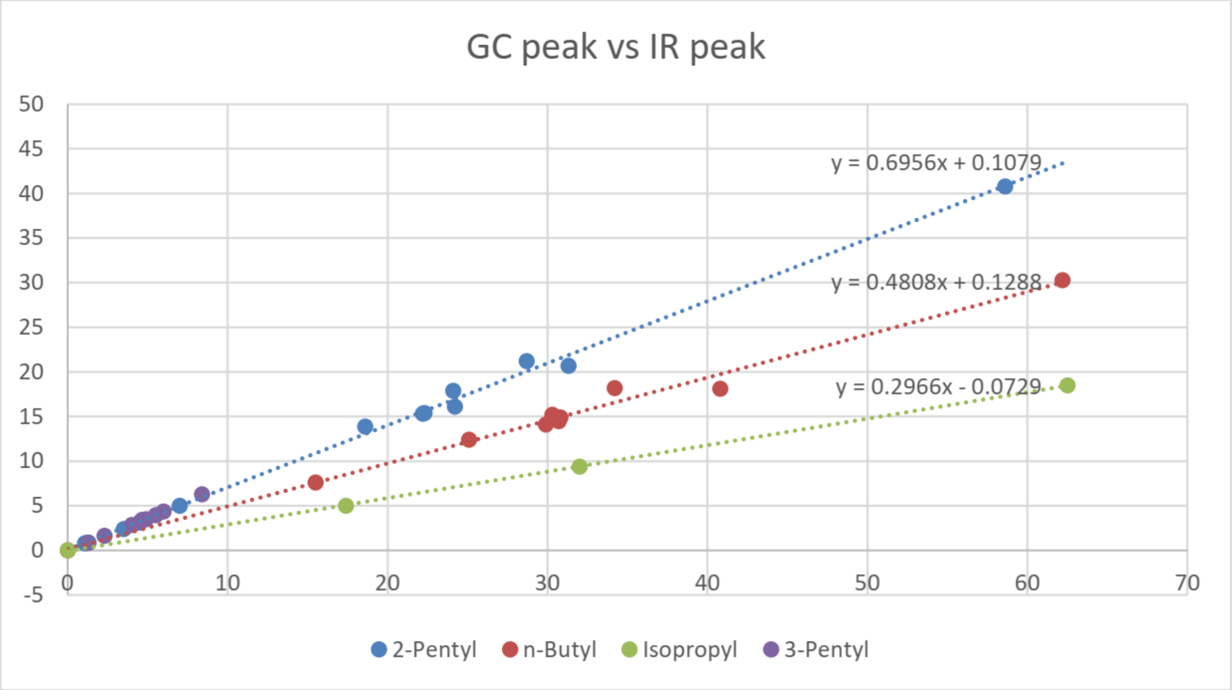

Figure 1: The response of the GC versus the integrated infrared area (both in arbitrary units). The IR sensitivity of the nitrates is assumed to be independent of the molecule, and so the slopes represent the size-dependence of the GC response.

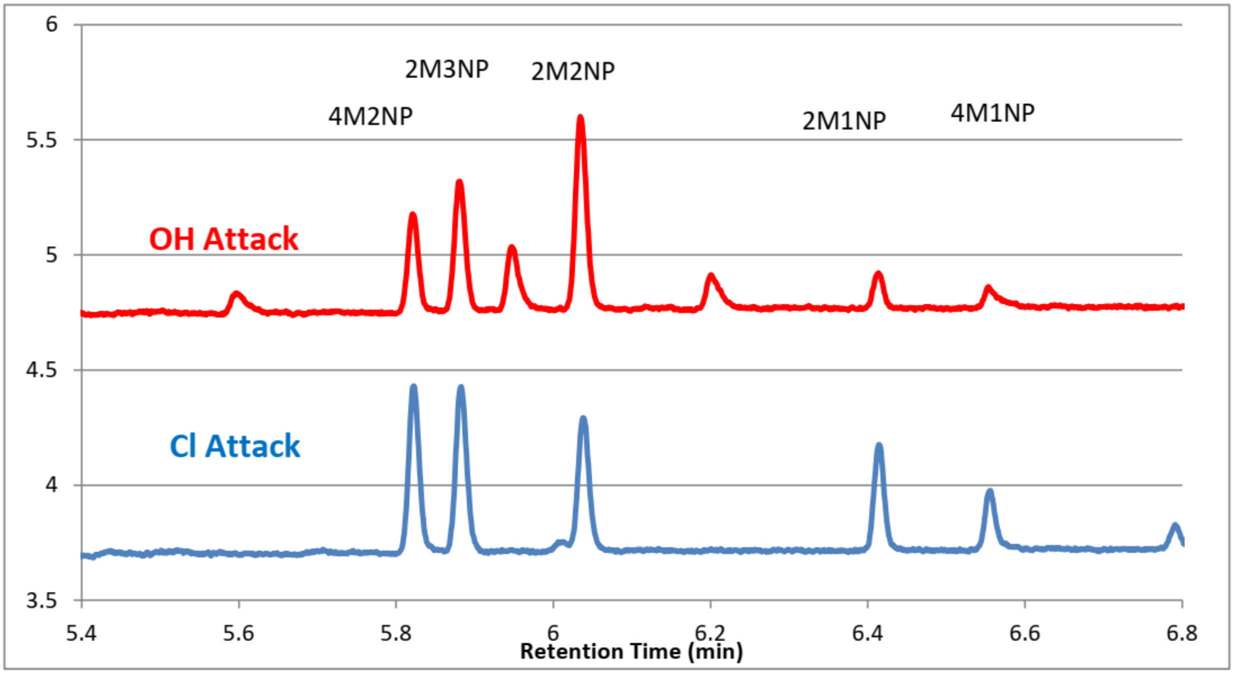

Figure 2: Chromatograms showing the production of nitrates in the reaction of OH radicals (upper trace) and chlorine atoms (lower trace) with 2-methyl pentane. The nitrate peaks are labeled according to the scheme 4M2NP = 4-methyl-2-nitrooxy pentane, etc. The correspondence of peaks in the two traces allows for positive identification of the nitrates. The tertiary peak (2M2NP) is clearly the largest peak in the OH reaction, and relatively much smaller in the Cl reaction.

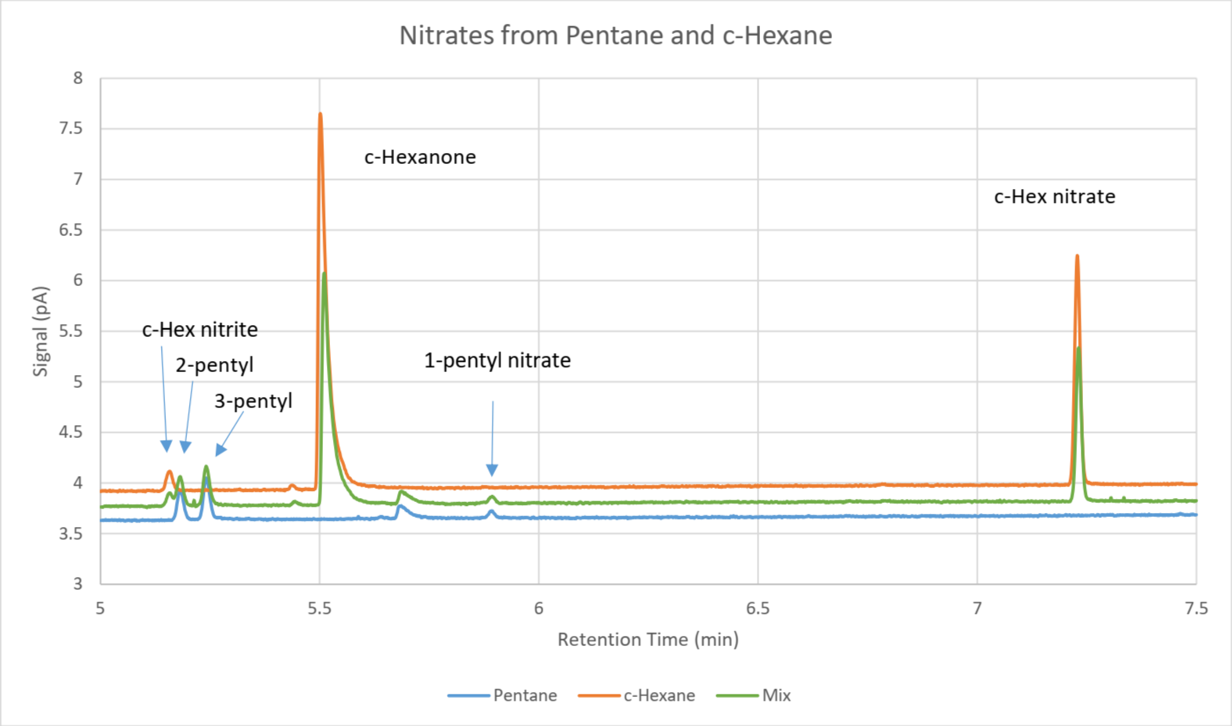

Figure 3: Composite showing the production of nitrates and other species from the OH-initiated oxidation of pentane (lower, blue trace), cyclohexane (upper, orange trace) and a mixture of the two compounds (middle, green trace). The initial concentrations were chosen such that the amount of each alkane converted in the mixed experiment was the same.

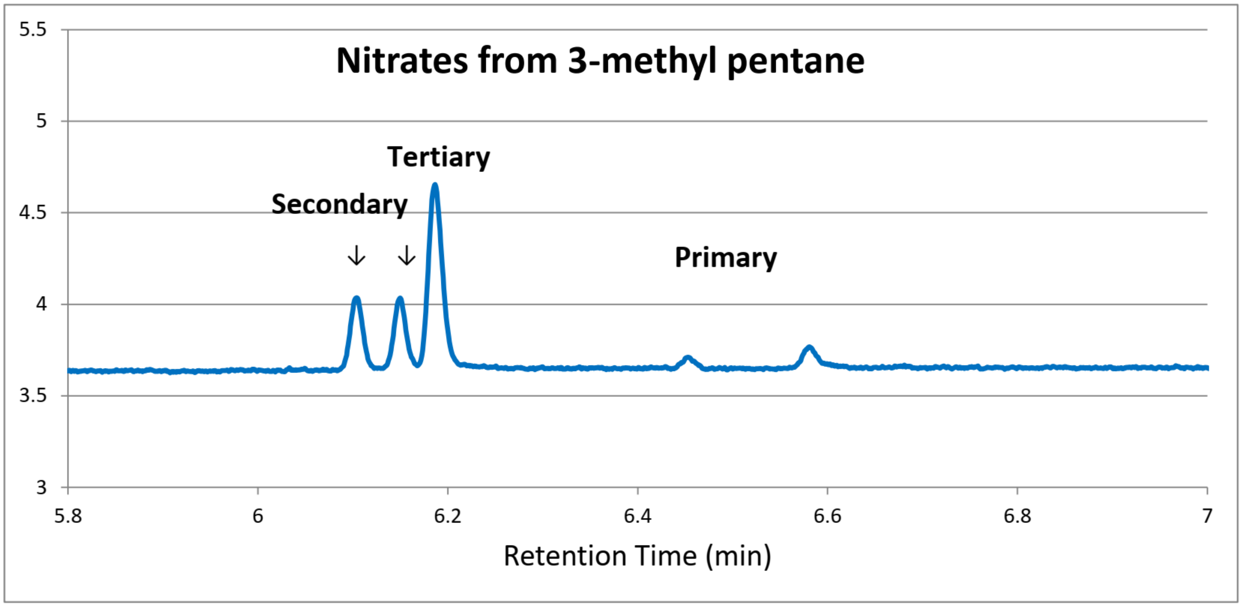

Figure 4: Gas chromatogram from the OH-initiated oxidation of 3-methyl pentane. The use of authentic samples confirmed that the first two peaks are diastereoisomers of the secondary nitrate, 3-methyl-2-nitrooxy pentane.

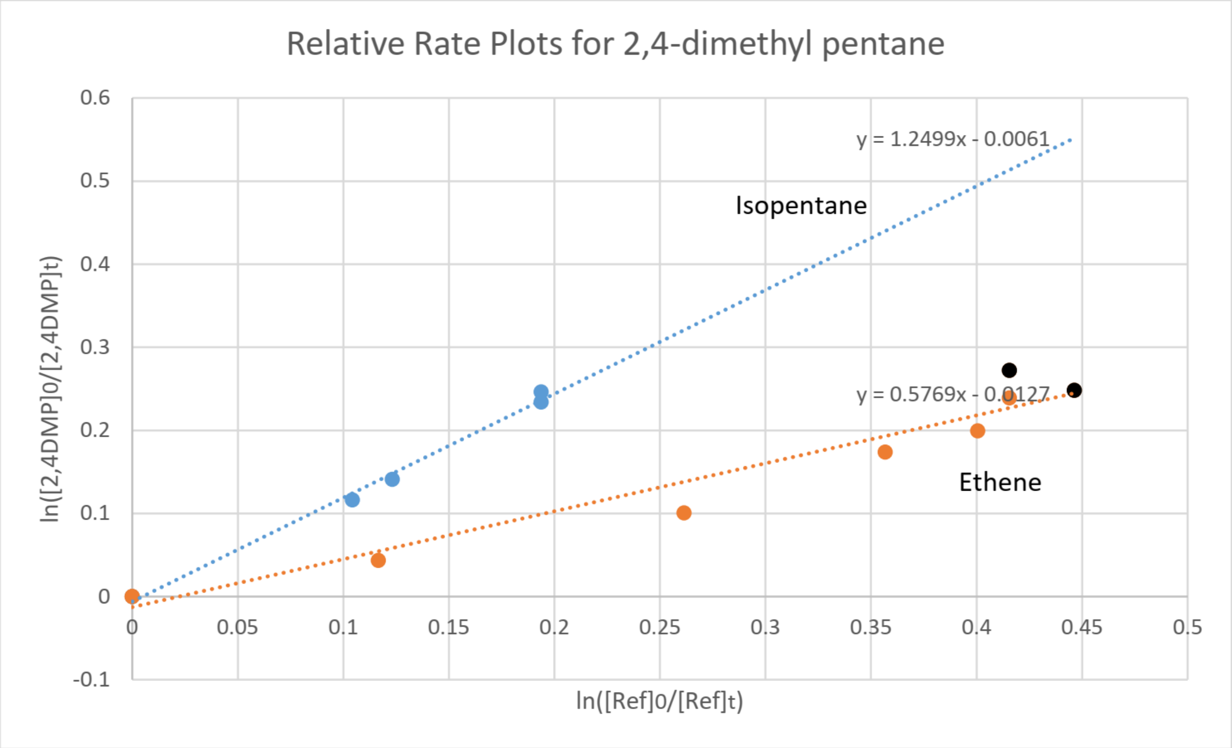

Figure 5: Relative rate plot for 2,4-dimethyl pentane versus isopentane (upper line) and ethene (lower line). The values versus isopentane are determined by GC (2 experiments). For ethene, the black points are determined by GC (2 experiments), while the orange points are from one series of IR spectra.

Table 1: Summary of Experimental Conditions

Reactant	Oxidant	T (°C)	P_0 (Torr)	O_2 (Torr)	[Alkane] $x10^{14}$	[NO] $x10^{14}$	Cl_2/i-PONO $x10^{14}$	Time (min)
Pentane	Cl	23	727	303	3.5	3.15	0.7	20
	Cl	23	727	303	3.5	3.15	0.77	32
	OH	23	717	305	3.5	3.5	3.64	50
	OH	23	721	306	3.5	3.5	3.92	50
	OH	23	717	300	3.5	3.5	3.5	50
	OH	-4	722	300	3.5	2.1+2.1	4.48	45+50
	OH	-23	721	450	3.5	2.1+2.1	4.2	45+30
Isopentane	Cl	23	761	300	3.5	2.94	0.77	26
	Cl	23	725	303	2.8	4.2	1.19	30
	Cl	23	725	304	3.5	4.2	1.75	24
	OH	23	725	300	3.5	4.2	3.5	20+25
	OH	23	724	300	3.5	2.8	3.5	40
	OH	23	721	300	3.5	4.2	7	50
	OH	23	707	300	3.5	1.4+2.1	3.5	16+28
	OH	23	707	300	3.5	2.45	3.5	40
	OH	23	717	304	3.5	2.8+2.1	4.2	40+45
	OH	23	717	306	3.5	2.8+1.4	3.5	30+30
	Cl	-4	723	300	3.5	2.8+2.8	2.1	16+20
	OH	-4	723	300	3.5	2.8+2.1	4.62	45+55
	OH	-4	718	300	3.5	2.1	5.32	80
	OH	-23	759	300	3.5	3.5	4.2	50
	OH	-23	722	300	3.5	2.4+2.1	4.69	45+60
	Cl	-23	760	300	3.5	2.8	1.75	25
	Cl[a]	-23	760	300	3.5	3.5	1.75	30

c-Hexane	Cl	23	732	300	3.5	3.5	21	2
	Cl	23	733	303	3.5	2.8	21	1
	Cl	23	721	300	3.5	2.66	10.5	2
	Cl	23	728	303	3.5	2.8	1.26	17
	Cl	23	728	322	3.5	3.15	0.7	24
	OH	23	726	305	3.5	2.8+2.4	3.43	35+35
	OH	23	721	311	3.5	2.8+1.8	3.43	22+38
	OH[b]	23	721	300	2.1	2.9+3.0	5.6	20+25
	OH	-4	723	300	3.5	2.8+2.1	3.5	50+40
	OH	-4	721	300	3.5	3.5	4.76	70
	Cl	-23	721	450	4.62	2.5+2.1	1.75	23+26
	Cl	-23	719	48	3.5	2.8+2.8	3.5	20+20
	OH	-23	723	302	3.5	2.8+2.1	5.6	45+30
3-Methyl Pentane	Cl	23	731	300	3.5	4.2	1.75	21
	Cl	23	723	298	2.8	2.38	0.84	22
	Cl	23	722	302	3.5	7	3.5	10+10
	OH	23	708	300	3.5	2.8+1.4	3.5	30+40
	OH	23	710	60	3.5	2.8+1.4	3.5	40+50
	OH[c]	23	727	300	2.1	3.5	4.06	45
	OH	23	724	302	3.5	2.8+1.5	3.5	34+29
	OH[c]	23	726	300	2.1	2.8+2.0	4.2	31+55
	OH[c]	23	721	300	2.1	3.5+2.8	4.62	40+40
	OH	23	723	300	3.5	2.1+2.1	4.41	28+30
	OH	-4	726	300	3.5	2.8	2.1	80
	OH	-4	720	300	3.5	2.8+2.1	4.69	35+25
	OH	-23	724	300	3.5	2.1+1.8	3.85	40+40
	OH	-23	719	300	3.29	2.1+2.1	4.2	41+40

2-Methyl Pentane	Cl	23	724	300	3.5	4.2	1.75	21
	Cl	23	725	300	2.8	2.45	1.05	17
	Cl	23	734	300	3.5	7	1.68	15+30
	OH	23	718	300	3.5	3.15	3.57	50
	OH	23	722	300	3.5	2.8+2.7	5.25	50+70
	OH	23	725	300	3.5	2.8+2.8	4.27	40+70
	OH[d]	23	721	300	2.1	3.0+2.8	4.9	40+55
	OH	-4	718	306	3.5	2.8+2.8	4.62	45+45
	OH	-4	721	303	3.5	2.8	3.15	55+45
2,4-Dimethyl Pentane	Cl	23	761	308	3.43	3.15	0.77	45
	Cl	23	759	300	3.5	14	10.5	15
	OH	23	721	305	3.5	3.1+2.8	3.92	35+45
	OH	23	722	305	3.5	2.8+2.5	3.5	30+40
	OH[e]	23	720	305	1.4	2.8+3.0	3.85	24+37
	OH[f]	23	736	252	1.4	4.2	8.4	47
	OH[f]	23	760	302	1.75	4.27	10.64	40
2,2,4-Trimethyl Pentane	Cl	23	722	300	3.5	2.8	2.1	13
	OH	23	714	300	3.5	2.8	3.43	55

The columns list: the alkane under study; the oxidant used in a given experiment (Cl or OH); the temperature; the initial pressure; the oxygen pressure; the initial concentration of alkane (molecule cm^{-3}); the initial and added NO (molecule cm^{-3}); the initial concentration of the photolytic precursor, Cl_2 or isopropyl nitrite (molecule cm^{-3}); and the total reaction time in minutes.

Footnotes.

a) Included 2.8×10^{14} molecule cm^{-3} NO_2.

b) Included 3.5×10^{14} molecule cm^{-3} pentane.

c) Included 2.9×10^{14} molecule cm^{-3} pentane.

d) Included 2.8×10^{14} molecule cm^{-3} pentane.

e) Included 2.1×10^{14} molecule cm^{-3} i-pentane (products and relative rate).

f) Included 2.8×10^{14} molecule cm^{-3} ethene (relative rate experiment)