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<th>Journal:</th>
<th>The Journal of Physical Chemistry</th>
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<td>Manuscript ID:</td>
<td>jp-2011-12136r</td>
</tr>
<tr>
<td>Manuscript Type:</td>
<td>Special Issue Article</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>15-Dec-2011</td>
</tr>
<tr>
<td>Complete List of Authors:</td>
<td>Sprague, Matthew; California Institute of Technology, Chemistry Garland, Eva; Agile Sciences, Moller, Andrew; The Aerospace Corporation, Bloss, Claire; Worcestershire County Council, Research and Intelligence Bean, Brian; Lando &amp; Anastasi, LLP, Weichman, Marissa; California Institute of Technology, Chemistry Mertens, Laura; California Institute of Technology, Chemistry Okumura, Mitchio; California Institute of Technology, Chemistry Sander, Stan; NASA/Jet Propulsion Laboratory, Lab Studies and Modeling</td>
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Kinetics of $n$-Butoxy and 2-Pentoxy Isomerization and Detection of Primary Products by Infrared Cavity Ringdown Spectroscopy

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ABSTRACT

The primary products of \( n \)-butoxy and 2-pentoxy isomerization in the presence and absence of \( O_2 \) have been detected using Pulsed Laser Photolysis – Cavity Ringdown Spectroscopy (PLP-CRDS).

Alkoxy radicals were generated by photolysis of alkyl nitrite precursors (\( n \)-butyl nitrite or 2-pentyl nitrite), and the isomerization products were detected by infrared cavity ringdown spectroscopy 20 \( \mu \)s after the photolysis. We report the mid-IR \( \nu_1 \) OH stretch absorption spectra for \( \delta \)-HOC\(_4\)H\(_8\)•, \( \delta \)-HOC\(_4\)H\(_8\)OO•, \( \delta \)-HO-1-C\(_5\)H\(_{10}\)•, and \( \delta \)-HO-1-C\(_5\)H\(_{10}\)OO•. The observed \( \nu_1 \) bands are similar in position and shape to their parent alcohols (\( n \)-butanol and 2-pentanol), although the HOROO• absorption is somewhat stronger than the HOR• absorption. We determined the rate of isomerization relative to reaction with \( O_2 \) for the \( n \)-butoxy and 2-pentoxy radicals by measuring the relative \( \nu_1 \) absorbance of HOROO• as a function of [\( O_2 \)]. At 295 K and 670 Torr of \( N_2 \) or \( N_2/O_2 \), we found rate constant ratios of \( k_{\text{isom}}/k_{O2} = (1.69 \pm 0.15) \times 10^{19} \text{ cm}^{-3} \) for \( n \)-butoxy, and \( k_{\text{isom}}/k_{O2} = (3.37 \pm 0.43) \times 10^{19} \text{ cm}^{-3} \) for 2-pentoxy (2\( \sigma \) uncertainty). Since isomerization is predicted to be in the high pressure limit at 670 Torr, these relative rates are expected to be the same at atmospheric pressure. Our results include corrections for prompt isomerization of hot nascent alkoxy radicals as well as reaction with background NO and unimolecular alkoxy decomposition. We estimate prompt isomerization yields under our conditions of 4 ± 2% and 5 ± 2% for \( n \)-butoxy and 2-pentoxy formed from photolysis of the alkyl nitrates at 351 nm. Our measured relative rate values are in good agreement with and more precise than previous end-product analysis studies conducted on the \( n \)-butoxy and 2-pentoxy systems. We show that reactions typically neglected in the analysis of alkoxy relative kinetics (decomposition, recombination with NO, and prompt isomerization) may need to be included in order to obtain accurate values of \( k_{\text{isom}}/k_{O2} \).

Keywords: volatile organic compounds, atmospheric chemistry, hydroxyalkylperoxy radical,
INTRODUCTION

Volatile organic hydrocarbons (VOCs) are released into the atmosphere in large quantities from both anthropogenic and biogenic sources. Once in the troposphere, VOCs are degraded through oxidation initiated by reaction with radicals, ozone, or photolysis. In these oxidative processes, alkoxy radicals (RO•) are often key intermediates that can react further via several mechanisms. The branching ratios of the various pathways determine the distribution of final oxidation products, and therefore influence how emitted VOCs contribute to the formation of ozone, smog, and secondary organic aerosols. 1-3

The oxidation of alkanes (denoted RH here) provides the simplest example of alkoxy radical chemistry. In the presence of NOx, alkoxy radicals are formed from alkanes in the troposphere predominantly by the following mechanism: 1-3

\[
RH + \cdot OH \rightarrow R \cdot + H_2O \tag{1}
\]

\[
R \cdot + O_2 \rightarrow RO_2 \cdot \tag{2}
\]

\[
RO_2 \cdot + NO \rightarrow RO \cdot + NO_2 \tag{3}
\]

The NO2 formed in this process undergoes photolysis in the troposphere to yield O atoms which subsequently react with O2 to generate ozone. The alkoxy radicals react further via one of three mechanisms: α-hydrogen abstraction by O2 to form a carbonyl and HO2, unimolecular isomerization involving a 1,5-hydrogen shift via a cyclic transition state, or unimolecular dissociation via β-scission. These three reactions for the n-butoxy radical (a primary alkoxy radical) and the 2-pentoxy radical (a secondary alkoxy radical) are shown below.
The computed energetics for the reactions of the \( n \)-butoxy radical are shown in Figure 1. The diagram is a composite of two different calculations, since no single consistent set of calculations exists for all available reaction paths. For the \( n \)-butoxy radical, Somnitz and Zellner\(^4,5\) calculated barriers for decomposition and isomerization of 15.0 kcal mol\(^{-1}\) and 10.2 kcal mol\(^{-1}\), respectively, at the modified
G2(MP2,SVP) level of theory. Jungkamp et al.\textsuperscript{6} calculate a barrier for reaction with O\textsubscript{2} of 8.2 kcal mol\textsuperscript{-1}, at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level of theory.

Many experimental and theoretical studies have shown that relative importance of the reaction pathways of alkoxy radicals depends critically upon the structure of the alkoxy radical. Several reviews are available.\textsuperscript{7-11} For all alkoxy radicals, unimolecular decomposition is an available pathway, and the rate of decomposition is faster when the transition state is stabilized through substitution at the \(\alpha\)- or \(\beta\)-carbon. Those alkoxy radicals containing an \(\alpha\)-hydrogen can also undergo hydrogen abstraction reaction with O\textsubscript{2}. Only radicals which can form a 6-membered ring transition state have a sufficiently low barrier for unimolecular isomerization to be atmospherically relevant,\textsuperscript{7,12-15} and the isomerization rate is fastest when the product is a secondary or tertiary alkyl radical.\textsuperscript{7} For molecules in which all three pathways are possible, isomerization and reaction with O\textsubscript{2} dominate under atmospheric conditions. Measurements of \(k_{O2}\) have generally yielded values within a factor of two of \(1 \times 10^{-14}\) cm\textsuperscript{3} molec\textsuperscript{-1} s\textsuperscript{-1} at 298 K, with small dependencies on temperature and the structure of the alkoxy radical.\textsuperscript{8,10} Variations in \(k_{\text{isom}}\) and \(k_{\text{decomp}}\) with pressure, temperature, and molecular structure are much larger, spanning many orders of magnitude because of the significant barriers involved and differences in the densities of states.\textsuperscript{16-25}

Isomerization has been a particularly difficult process to study experimentally due to the wide range of values of \(k_{\text{isom}}\) and fast secondary chemistry. In molecules which can form a 6-membered ring, isomerization generally occurs on the timescale of microseconds or less. In addition, the primary products of isomerization are hydroxyalkyl radicals with fast secondary reaction rates. As a result, the isomerization of alkoxy radicals has not yet been observed directly. Many previous studies of \(k_{\text{isom}}\) have focused on the simplest alkoxy radicals that can undergo isomerization: \(n\)-butoxy, 1-pentoxy, and 2-pentoxy. Under conditions relevant to the lower atmosphere (300K, 1 bar, 21% O\textsubscript{2}) the lifetime for reaction with O\textsubscript{2} is on the order 20 \(\mu\)s.\textsuperscript{26} Previous relative rate measurements have estimated the lifetimes for isomerization under these conditions to be on the order of 3 \(\mu\)s for reaction (5) and shorter.
The decomposition reactions have been estimated to occur on longer timescales: on the order 1 ms for reaction (6) and 100 μs for reaction (9). As a result, isomerization and reaction with \( \text{O}_2 \) are expected to be the dominant fates for these alkoxy radicals.

Most previous experimental measurements have been conducted in static smog chambers or slow-flow gas kinetic cells in which the concentrations of end-products were measured. \(^{13, 15, 27-32}\) Alkoxy radicals were produced through generation of the corresponding alkyl radical followed by reactions (2)-(3) or by UV photolysis of the corresponding alkyl nitrite. The relative rate constants for isomerization to reaction with \( \text{O}_2 \) \((k_{\text{isom}}/k_{\text{O}_2})\) were estimated by measuring the concentrations of end-products as a function of oxygen pressure.

In the presence of \( \text{O}_2 \), the \( \delta \)-hydroxyalkyl radicals formed in reactions (5) and (8) rapidly associate with \( \text{O}_2 \) to form \( \delta \)-hydroxyalkylperoxy radicals, reactions (10) and (11).

\[
\begin{align*}
\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{OH} + \text{O}_2 & \xrightarrow{M} \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{O}_2\text{OH} \quad (10) \\
\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{OH} + \text{O}_2 & \xrightarrow{M} \text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3\text{O}_2\text{OH} \quad (11)
\end{align*}
\]

Under boundary layer conditions, these association reactions are completed within 50 ns. Most prior experiments have included NO. In this case the products of reactions (10) and (11) react with NO via reaction (3) to generate a secondary alkoxy radical. This secondary alkoxy radical can also undergo reaction via several pathways, leading to a large variety of possible end-products. Often, several reaction pathways can generate the same products, and so it can be difficult to deduce reaction mechanisms by relying on end-product data. \(^6\)

Hein \textit{et al.} made the only measurement of \( k_{\text{isom}} \) which did not rely on end product analysis. \(^{33}\) They measured the secondary production of \( \text{OH} \) and \( \text{NO}_2 \) in steady state using laser-induced
fluorescence (NO\textsubscript{2}) and long-pass absorption spectroscopy (OH), and then fit their observed time profiles using a kinetic model. While this was a more direct real-time measurement of the isomerization kinetics, the steady state analysis still relied upon an accurate knowledge of secondary kinetics, and measurements were limited to low-pressures (50 mbar), well below the high pressure limit.

An additional concern in studying the reaction pathways of alkoxy radicals is the possibility of preparing vibrationally excited alkoxy radicals. Hot alkoxy radicals can be formed from excess nitrite photolysis energy or the exothermicity of reaction (3). Some of this energy is distributed in the vibrational modes of the alkoxy radicals. Vibrationally hot alkoxy radicals could undergo prompt isomerization (reaction 12) or prompt decomposition (reaction 13) before becoming thermalized by collisional energy transfer:

\[
\text{RO}^* \xrightarrow{\text{prompt}} \text{HOR}^* \quad (12)
\]

\[
\text{RO}^* \xrightarrow{\text{prompt}} \text{R}^* + \text{HCHO} \quad (13)
\]

Two previous experiments have examined the possibility of rapid chemical activation by hot alkoxy radicals. Geiger \textit{et al.} prepared \textit{n}-butoxy radicals from 254 nm photolysis of an \textit{n}-butyl iodide/O\textsubscript{2}/NO/N\textsubscript{2} mixture, and noted that their observed oxygen-dependence on \(k_{\text{isom}}/k_{O2}\) was best explained by the presence of 10-20\% hot butoxy radicals. \textsuperscript{34} Cassanelli \textit{et al.} prepared \textit{n}-butoxy radicals by photolyzing \textit{n}-butyl nitrite at 370 ± 10 nm (FWHM) and estimated a 10\% yield of product due to non-thermal prompt isomerization. \textsuperscript{35}

In contrast to previous studies, detection of the primary products of alkoxy radical reactions in real time provides a more direct means of examining these reactions that is less affected by secondary reactions. We have shown that pulsed Infrared Cavity Ringdown Spectroscopy (IR-CRDS) provides a sensitive means for detecting transient intermediates in flow cell experiments. \textsuperscript{36,37} CRDS utilizes a high finesse optical cavity to measure very small absorbances and is an increasingly popular method for the monitoring of trace species. \textsuperscript{8,38-41} In principle, pulsed IR-CRDS detection provides a general method for
detecting a wide range of intermediates with a time resolution of approximately 10-100 μs, with the time resolution limited by the ringdown measurement time.

Numerous spectroscopic studies on the alkoxy radicals themselves have been carried out, typically employing laser induced fluorescence to measure the A-X or B-X electronic transitions. However, fluorescence is quenched for larger alkoxy radicals due to internal conversion.

The primary products from alkoxy radical isomerization have not been detected spectroscopically. The products formed in the absence and presence of O₂, the hydroxy-alkyl (HOR•) and hydroxy-alkyl-peroxy radicals (HOROO•) respectively, both contain a hydroxyl group. The infrared spectra of these radicals will feature a characteristic OH stretch absorption at approximately the same frequency as the corresponding alcohol (denoted ROH). On short enough timescales (<20 μs) the OH stretch spectrum can be a unique measure of the primary alkoxy isomerization products.

In this work, we directly detect the primary products of n-butoxy and 2-pentoxy isomerization using IR-CRDS. We report the ν₁ (OH stretch) vibrational spectra of δ-HOC₄H₈•, δ-HOC₅H₈OO•, δ-HO-1-C₅H₁₀•, and δ-HO-1-C₅H₁₀OO•. We use Pulsed Laser Photolysis (PLP) of alkyl nitrite precursors to generate the relevant alkoxy radicals, RO•, and then detect vibrational spectra of the products by IR-CRDS on the 20 μs timescale. We take advantage of the fact that isomerization is the only primary reaction pathway for these alkoxy radicals to form a hydroxyl group (-OH), therefore making the spectral bands unique to the isomerization products. The ν₁ bands were then used to determine the relative kinetics of alkoxy isomerization and reaction with O₂ for n-butoxy and 2-pentoxy, and the extent of prompt decomposition and isomerization of hot alkoxy radicals formed in our experiment. We also show that the effects of other reactions of alkoxy radicals (decomposition, reaction with NO, and prompt processes) must be included in alkoxy relative kinetics analyses.

**EXPERIMENTAL**
Our PLP-CRDS experimental setup consisted of a laminar flow photolysis cell in which alkyl nitrite precursors were photolyzed with an excimer laser to generate alkoxy radicals (Figure 2). These experiments were performed at room temperature and a pressure of either 300 Torr (spectroscopy) or 670 Torr (kinetics), with mixtures of O\textsubscript{2} and N\textsubscript{2} used as bath gases. The photolysis repetition rate was 10 Hz, and the gas mixture was flushed out of the cell every 25 ms (spectroscopy) or 75 ms (kinetics), so that a fresh gas sample was probed with each laser pulse. Typical experimental conditions can be found in Table 1.

The reaction products were probed with infrared cavity ringdown spectroscopy (IR-CRDS) using infrared light 2.7-3.7 µm and mirrors with a peak reflectivity of 99.98%. Pulsed infrared radiation from 2.7-3.7 µm was generated with a dual potassium titanyl phosphate (KTP) crystal optical parametric amplifier (OPA)\textsuperscript{63} at the difference frequency between the outputs of a doubled YAG (532 nm) and a tunable dye laser (620-665 nm). Products were detected 20 µs after photolysis in order to minimize effects of secondary chemistry.

Infrared spectra of alkoxy radical reaction products were collected with the excimer on and excimer off at each frequency. The signal with the excimer off (with no alkoxy radical formation) was subtracted to eliminate background from precursor gases and changing mirror reflectivity. The nitrite precursors contributed background absorption in the mid-IR region of interest (3610-3720 cm\textsuperscript{-1}), roughly 5 times the signal due to products. Infrared spectra of the isomerization products HOR• and HOROO• were obtained by scanning from 3610-3720 cm\textsuperscript{-1} with a 0.2 cm\textsuperscript{-1} step size. Within 20 µs, isomerization is the only alkoxy reaction pathway expected to produce hydroxyl groups, the only functional group contributing to the bands observed in these regions.

*Generation of pulsed infrared radiation – OPA (2.7 – 3.7 µm)*
Pulsed infrared radiation from 2.7 – 3.7 µm was produced with an OPA (Figure 3), based on the configuration reported by Reid.\(^6\) With typical input energies of 150 mJ of pump radiation (532 nm) and 5 mJ of signal radiation (620-665 nm), the OPA produced 1 mJ of idler (infrared) radiation with a linewidth of 1 cm\(^{-1}\). Potassium titanyl phosphate (KTP) crystals were used for the OPA because of their relatively high damage threshold (>250 MW/cm\(^2\)). The crystals were cut at 44° off the z-axis in the xz plane, with 7 mm x 7 mm crystal faces, and were 15-mm long (Crystal Technologies). Two KTP crystals were used in series in order to obtain a higher conversion of pump to signal and idler radiation and to compensate for beam displacement as the crystals were angle tuned. The angle of each KTP crystal was set by a stepper motor mounted on a translation stage controlled by a LabVIEW program; the program controlled the movement of the two stepper motors that adjusted the angles of the OPA crystals to maintain phase matching as the dye wavelength was scanned.

The pump beam consisted of 532 nm radiation produced by doubling the output of a Nd:YAG laser (Quantel YG-661 or Continuum Surelite III). Approximately 50% was diverted to pump a dye laser (Spectra Physics PDL3), which produced the signal radiation. The pump beam then passed through a delay line, the length of which was adjusted to optimize the temporal overlap of the pump and signal beams at the OPA. The polarization of the pump beam was then adjusted with a half wave plate so that it entered the OPA parallel to the plane of the laser table. The dye laser produced the signal beam with vertical polarization, and the output wavelength could be varied from 620 to 665 nm with DCM dye. Both the pump and signal beams were reduced with telescoping optics to approximately half of their original diameter before being combined with a dichroic beam combiner and sent into the OPA.

After passing through the OPA, the green and red beams were separated from the IR by sapphire optics with anti-reflective coatings centered at 532 nm and 630 nm. Remaining traces of the red and green light were eliminated by passing the beams through a polished silicon optic placed at Brewster's angle (74°) to maximize transmission of the IR radiation. The resulting IR power varied from...
0.4 – 1.0 mJ depending on frequency. An 85-cm focal length CaF$_2$ lens was placed in front of the ringdown cell to focus the IR light at the center of the cell.

**Generation of Alkoxy Radicals via Photolysis**

Alkoxy radicals were photolyzed in situ from their nitrite precursors with the output beam from an excimer laser (Lambda Physik LPX 210i) at 351 nm:

\[ \text{RONO} + h\nu \rightarrow \text{RO}^\bullet + \text{NO} \quad (14) \]

Nitrogen was bubbled through the liquid alkyl nitrites (kept at 0 °C) in order to introduce them into the reaction cell. The concentration of alkyl nitrites was determined by an absorption measurement of the N$_2$/alkoxy nitrite flow using the 254 nm emission from a mercury lamp. The absorption cross section of methyl nitrite at 254 nm is $1 \times 10^{-18}$ cm$^2$, and the cross section for the other alkyl nitrites is expected to be similar.\textsuperscript{64,65} Alkyl nitrite concentrations in the reaction cell were kept as low as possible, [RONO] = (7 – 15) × 10$^{15}$ molec cm$^{-3}$, because they absorbed infrared radiation broadly in the range 3300-3800 cm$^{-1}$ range giving rise to a background which had to be subtracted and which reduced our spectroscopic sensitivity for detecting products.

All butyl nitrite precursors were purchased from Aldrich (95% purity). 2-pentyl nitrite was synthesized from pentanol in aqueous sodium nitrite, using a modification of the synthesis of 1-butyl nitrite described in Organic Syntheses Vol. 2.\textsuperscript{66} Briefly, a cold mixture of sulfuric acid and 2-pentanol was added slowly to a cold aqueous solution of sodium nitrite. The crude product was distilled to reduce the amount of excess residual 2-pentanol. Based on FTIR spectra of the distilled 2-pentyl nitrite, the ratios of major contaminants to 2-pentyl nitrite were: water, 1:14; 2-pentanol, 1:24; NO, 1:240. Both alkyl nitrites were freeze-pumped immediately before use to remove volatile impurities. Nitrogen and oxygen were used as bath gases. We chose [O$_2$] = 1 × 10$^{18}$ molec cm$^{-3}$ to acquire the HOROO$^\bullet$ spectra to ensure that all of the isomerization product was converted from HOR$^\bullet$ to HOROO$^\bullet$ (reactions 10 and 11) while
keeping competition from the alkoxy + O₂ channel low (reaction 7). Typical experimental conditions are listed in Table 1. Gas flow rates were measured with mass flowmeters (Omega, Edwards) calibrated volumetrically. Gases were mixed in a glass cross 5 cm upstream from the photolysis region.

Alkyl nitrites were photolyzed by operating the excimer laser at 351 nm. At this wavelength, the typical output energy was 160 mJ per pulse. The output beam, initially 3 cm × 1 cm, was focused vertically and expanded radially so that the resulting beam at the cell was 5 cm × 0.3 cm, collimated in the vertical axis and slightly divergent horizontally. The flux of photons entering the cell was 2 × 10^{17} photons cm⁻² resulting in approximately 1.5% photolysis of the nitrite precursors (σ_{351 nm} = 8 × 10^{-20} cm² molec⁻¹). Care was taken not to focus the excimer beam too tightly on the PLP cell, as this caused soot to burn onto the windows and photoacoustic peaks with a period of roughly 20 µs to appear in the kinetics scans. By defocusing the excimer beam slightly, this effect was eliminated. A single experiment was run operating the excimer laser at 248 nm with the following parameters: typical energy 125 mJ per pulse, beam area entering cell 3 cm × 1 cm, flux 5 × 10^{16} photons cm⁻², 7% photolysis of nitrite precursors (σ_{248 nm} = 1.3 × 10^{-18} cm² molec⁻¹).

The timing of the excimer and YAG lasers was controlled by digital delay generators (Stanford Research Systems DG535). This set the time delay between the formation of the initial alkoxy radicals (via photolysis) and the detection of products with cavity ringdown spectroscopy. The spectra presented in this paper were collected by keeping the photolysis-probe delay constant (20 µs) and scanning in frequency space. Direct measurement of chemical kinetics was made by holding the IR wavelength fixed and varying the photolysis-probe delay. In either configuration, ringdown traces were collected at each point with the excimer on and with the excimer off. The frequency-dependent background arising from absorption by precursor gases and mirror reflectivity could then be subtracted.

**PLP Flow Cell with Cavity Ringdown Detection**
A schematic of our PLP-CRDS flow cell is shown in Figure 2. The cell consisted of a 7 cm × 1 cm metal rectangular tube, coated with a fluoropolymer (FluoroPel PFC 801A/coFS) to minimize reactions at the walls. Fused silica windows of 6 cm length were placed on two sides of the cell to allow light from an excimer laser to pass through. The cell was coupled to ringdown mirrors via Teflon blocks, which contained ports for introducing reactant gases and measuring the cell pressure.

The ringdown mirrors, which had their peak reflectivity of 99.98% at 2.8 µm (Los Gatos Research), were mounted in mirror housings, purged with nitrogen to prevent reactive chemicals from reaching and damaging the mirror surfaces. This purged volume included a 24-cm long glass tube between the ringdown mirror housing and the Teflon blocks of the photolysis cell.

The output radiation from the ringdown cavity was focused onto a liquid nitrogen cooled InSb detector (EG&G Judson) with a 5 cm focal length CaF\(_2\) lens. The signal was passed through a voltage amplifier (Analog Modules 351A), a high frequency filter and a ferrite choke, and then was digitized by a 14-bit PC oscilloscope board (GageScope CS1450). Ringdown data were collected for 80 µs after the Nd:YAG laser fired, at a rate of 25 MSa s\(^{-1}\). Ringdown traces from 16 shots were averaged and then fit to an exponential decay using the Levenberg-Marquardt algorithm. In order to reduce the effects of noise near the peak of the ringdown decay curve, only data after the first 12.5% of the calculated lifetime were used, and the lifetime was fit again. Typical empty cell ringdown times were on the order of 7 µs. The standard deviation of the mean of successive ringdown times obtained for an empty cell was typically 0.4%, giving a minimum detectable absorbance of 2.6 ppm per pass Hz\(^{1/2}\). In the presence of the alkyl nitrite precursor, typical ringdown times were on the order of 5 µs (spectra) or 3 µs (relative kinetics). The standard deviation of successive ringdown times was typically 0.4%, giving a minimum detectable absorbance of 3.6 ppm per pass Hz\(^{1/2}\) (spectra) or 6.1 ppm per pass Hz\(^{1/2}\) (relative kinetics).

**Experimental Conditions**
Typical conditions for both the spectroscopy and relative kinetics experiments are summarized in Table 1. Experiments were performed at room temperature (295K), at a pressure of 300-315 Torr (spectra) or 670 Torr (relative kinetics). Spectra were recorded with a 0.2 cm\(^{-1}\) interval between successive data points over the range 3620-3720 cm\(^{-1}\) (n-butoxy) or 3610-3710 cm\(^{-1}\) (2-pentoxy).

\([C_4H_9ONO]\) was kept at \(7 \times 10^{15}\) molec cm\(^{-3}\) for \(\delta\)-HOC\(_4\)H\(_8\)• and \(\delta\)-HOC\(_4\)H\(_8\)OO• spectra or \(1 \times 10^{16}\) molec cm\(^{-3}\) for n-butoxy relative kinetics, based on its vapor pressure (20 Torr at 273 K)\(^{67}\) and the gas flows used. To the best of our knowledge, the thermodynamic properties of 2-pentyl nitrite (vapor pressure, boiling point) are not available in the literature. We report the vapor pressure of our 2-pentyl nitrite sample as a function of temperature in the Appendix. \([C_5H_{11}ONO]\) was kept constant for each 2-pentoxy experiment, and was estimated to be \(7 \times 10^{15}\) molec cm\(^{-3}\) for \(\delta\)-HO-1-C\(_5\)H\(_{10}\)• and \(\delta\)-HO-1-C\(_5\)H\(_{10}\)OO• spectra and \(1 \times 10^{16}\) molec cm\(^{-3}\) for 2-pentoxy relative kinetics).

With 160 mJ/pulse of 351 nm light from the excimer, 1.5% photolysis of the butyl nitrite is expected, giving an initial \([C_4H_9O•]\) of \(1 \times 10^{14}\) molec cm\(^{-3}\). The photolysis cross section of 2-pentyl nitrite is unknown. Taking the cross section to be the same as for \(n\)-butyl nitrite (1.5% photolysis), we expect an initial \([C_5H_{11}O•]\) = \(1 \times 10^{14}\) molec cm\(^{-3}\). \([O_2]\) was set to 0 Torr for acquisition of HOR• spectra, and \(1 \times 10^{18}\) molec cm\(^{-3}\) for acquisition of HOROO• spectra. In order to maintain a constant pressure, \(O_2\) was replaced with \(N_2\) for experiments with \([O_2]\) = 0 Torr. The gas residence time inside the PLP cell was 25 ms (spectra) or 75 ms (relative kinetics), so that each laser shot probed a fresh sample of gas.

RESULTS

We present the results of our study in five parts. First, we first discuss the series of reactions that occurs following the photolysis of the alkyl nitrite precursor in the absence and presence of \(O_2\). We show that under our experimental conditions, secondary chemistry of the alkoxy isomerization products does not affect our experiments. Second, we present the cavity ringdown spectra. Based on the
chemistry discussed in the first part, we assign our observed IR peak to the $\nu_1$ mode (OH stretch) of the isomerization products of the alkoxy radical, HOR• and HOROO• in the absence and presence of O2, respectively. Third, we show that the $\nu_1$ band grows in too quickly to measure alkoxy isomerization kinetics directly at room temperature. Fourth, we use our IR spectra to estimate the prompt decomposition yield of the alkoxy radicals following photolysis of the alkyl nitrites at 248 nm and 351 nm by measuring the isomerization and decomposition products simultaneously. Fifth, we derive a relationship between the $\nu_1$ absorbance and [O2], present our relative kinetics measurements, and calculate the relative rate $k_{\text{isom}}/k_{\text{O2}}$ for n-butoxy and 2-pentoxy. We show in this section that alkoxy reactions that are typically neglected in relative kinetics analyses (decomposition, recombination with NO, and prompt isomerization) have a small but detectable effect on the calculated $k_{\text{isom}}/k_{\text{O2}}$, and we apply the appropriate correction.

**Chemistry**

Photolysis of the alkyl nitrites in the UV leads to prompt dissociation, with a reaction enthalpy of 42 kcal mol$^{-1}$. 68

$$\text{RONO} + h\nu \rightarrow \text{RO•} + \text{NO}.$$  \hspace{1cm} (14)

For photolysis at 351 nm, the fragments contain 39 kcal mol$^{-1}$ of available energy. The observations by Bruhlmann et al. 69 and Mestdagh et al. 70 of anisotropic product angular distributions in the photolysis of alkyl nitrites indicates that products are formed on timescales less than a rotational period (< 1 ps). RO• and NO are formed almost exclusively, most likely on the excited RONO electronic surface, with a minor channel leading to OH production. 71 If we assume that the quantum yield for dissociation is $\phi_{d} = 1$, then for our laser fluence ($2 \times 10^{17}$ photons cm$^{-2}$ at 351 nm), we expect $[\text{C}_4\text{H}_9\text{O•}]_0 = 1 \times 10^{14}$ molec cm$^{-3}$. At 300 Torr, vibrational relaxation will lead to thermal equilibrium on timescales $<< 1$ µs. Based on
rate constants from the literature, isomerization for \(n\)-butoxy and 2-pentoxy radicals is expected to occur on time scales of 4 µs (\(k_{\text{isom}} = 2.5 \times 10^5 \text{ s}^{-1}\))

\[
\text{RO}^\bullet \longrightarrow \text{HOR}^\bullet
\]

(15)

while decomposition occurs on time scales of 2 ms for \(n\)-butoxy (\(k_{\text{decomp}} = 600 \text{ s}^{-1}\)) and 50 µs for 2-pentoxy (\(k_{\text{decomp}} = 2 \times 10^4 \text{ s}^{-1}\)). At the radical concentrations under these conditions, \([\text{RO}^\bullet] = [\text{NO}] = 1 \times 10^{14} \text{ molec cm}^{-3}\), recombination reactions of \(\text{RO}^\bullet\) with \(\text{NO}\) or \(\text{RO}^\bullet\)

\[
\text{RO}^\bullet + \text{RO}^\bullet \longrightarrow \text{ROOR}, \text{ other products}
\]

(16)

\[
\text{RO}^\bullet + \text{NO}^\bullet \longrightarrow \text{RONO}
\]

(17)

are approximately two orders of magnitude slower than isomerization (\(k_{\text{NO}} \times [\text{NO}] = 3000 \text{ s}^{-1}\)). Thus, isomerization (reaction 10) or the competing reaction with \(\text{O}_2\) to form \(\text{HO}_2\) and the respective aldehyde or ketone (reaction 11) will be the dominant fate of the alkoxy radicals.

In the absence of \(\text{O}_2\), the fate of the isomerization products, the hydroxy-alkyl radicals \(\text{HOR}^\bullet\), is either self-association or recombination with \(\text{NO}\).

\[
\text{HOR}^\bullet + \text{HOR}^\bullet \longrightarrow (\text{HOR})_2, \text{ other products}
\]

(18)

\[
\text{HOR}^\bullet + \text{NO}^\bullet \longrightarrow \text{HORNO}
\]

(19)

If we assume that the \(\text{HOR}^\bullet + \text{HOR}^\bullet\) association reactions are in the high pressure limit with rate constant \(5 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), a rate constant similar to both \(\text{HOCH}_2\)\(^\bullet\) self-reaction and \(\text{HOC}_3\text{H}_4\)\(^\bullet\) self-reaction, \(^{72}\) then the initial lifetime for reaction 18 is 200 µs. The rate constant for reaction 19 is unknown: analogous reactions have rate constants ranging from \(6 \times 10^{-14} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) (\(\text{C}_3\text{H}_7\)\(^\bullet\) + \(\text{NO}\)) to \(2 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) (\(\text{HOCH}_2\)\(^\bullet\) + \(\text{NO}\)). For \([\text{NO}] = 1 \times 10^{14} \text{ molec cm}^{-3}\), we obtain \(k_{19} \times [\text{NO}] = (6 – 2000)\) \(\text{s}^{-1}\), or lifetimes of (0.5 – 170) ms. Regardless of the exact value of the rate constant for \(\text{HOR}^\bullet + \text{NO}\), the reaction is at least two orders of magnitude less important than isomerization, and \([\text{HORNO}]\) can be considered negligible at 20 µs. Thus, at 20 µs, most (>90%) of the primary products will be \(\text{HOR}^\bullet\)
monomers, with a small fraction dimerizing to form HORROH. The reaction rate for association with NO (reaction 19) is too small to expect an appreciable contribution from HORNO. Similarly, a negligible amount of HOR• may have undergone hydrogen abstraction by NO to form butanol and a hydroxy-butene.

In the presence of O₂, the hydroxy-alkyl radicals HOR• will associate to form peroxy radicals HOROO• with a rate coefficient of roughly $7 \times 10^{-12}$ cm³ molec⁻¹ s⁻¹. 73

\[
\text{HOR}^\bullet + \text{O}_2 \xrightarrow{M} \text{HOROO}^\bullet
\]  (20)

There is probably a minor channel to form HO₂ and a hydroxylated alkene. 74 At 1 Torr of O₂, the pseudo-first order lifetime of HOR• is 5 µs. However, in most of our spectroscopy experiments, [O₂] = 30 Torr. Under these conditions, the pseudo-first order lifetime of HOR• is only 150 ns. Thus, all of the HOR• will have been converted to HOROO•.

Further reaction of HOROO• with NO will give a hydroxyalkoxy (HORO•) and NO₂ (reaction 21), with a rate coefficient of approximately $9 \times 10^{-12}$ cm³ molec⁻¹ s⁻¹. A minor association channel also exists, giving the hydroxyalkylnitrate HORONO₂ (reaction 22), with a rate coefficient of approximately $4 \times 10^{-13}$ cm³ molec⁻¹ s⁻¹. 11

\[
\text{HOROO}^\bullet + \text{NO} \rightarrow \text{HORO}^\bullet + \text{NO}_2
\]  (21)

\[
\text{HOROO}^\bullet + \text{NO} \rightarrow \text{HORONO}_2
\]  (22)

At the low NO concentrations generated from the photolysis of precursor (1 × 10¹⁴ molec cm⁻³), the pseudo-first order lifetime of HOROO• for reaction with NO is on the order 1 ms: too long to be of importance. Assuming that the rate constant for the HOROO• self-reaction is comparable to that for n-C₄H₉OO• self-reaction ($4 \times 10^{-13}$ cm³ molec⁻¹ s⁻¹), 75 no appreciable reaction of HOROO• will occur in less than 1 ms.

The above analysis shows that 20 µs after alkoxy radical formation, the effects of secondary chemistry are minimal, and the measured spectra should consist primarily of HOR• and HOROO•. To
further confirm this, we constructed a kinetics model using rate constants available in the literature with the Kintecus kinetics modeling software. We expect that with $[O_2] = 0$ Torr, the cavity ringdown spectrum 20 µs after RONO photolysis will be of HOR• (94%) and its dimer HORROH (6%). With $[O_2] = 1 \times 10^{18}$ molec cm$^{-3}$, the measured spectrum should be >98% HOROO•.

**Spectra**

Figures 4-7 show a series of infrared spectra obtained following the photolysis of various alkyl nitrite precursors. All spectra shown were taken with a photolysis-probe delay of 20 µs, with a 0.2 cm$^{-1}$ step size. The spectra presented in Figure 4 show the absolute cavity loss; the mirror reflectivity and absorption by the background gases have not been subtracted. Figures 5-7 have had the background spectra in the absence of photolysis (excimer-off) subtracted. Spectra were also collected for photolysis-probe delays over the range 10 - 800 µs. Figure 8 shows the time dependence of the absorbances observed in Figures 5 and 6. The spectra at 10 µs were weaker by a factor of 2 while spectra beyond 20 µs did not change in intensity, indicating that reactions to form HOR• and HOROO• went to completion by 20 µs.

Figure 4 shows the background IR spectra of the reactants (excimer-off) and the IR spectra of the background plus signal (excimer-on) for $n$-butyl nitrite (Figure 4a) and 2-pentyl nitrite photolysis (Figure 4b). Two species contribute to the background in both spectra: the parent alkyl nitrites (broad, structured absorption across the range 3610-3720 cm$^{-1}$) and water (sharp features at 3630 cm$^{-1}$, 3650 cm$^{-1}$, 3670 cm$^{-1}$, and 3690 cm$^{-1}$). In the 2-pentyl nitrite spectrum, an additional broad, structureless absorption from 2-pentanol is observed at 3660 cm$^{-1}$.

Following photolysis, new absorption bands are observed, centered near 3675 cm$^{-1}$ in the $n$-butyl nitrite spectrum and 3660 cm$^{-1}$ for the 2-pentyl nitrite spectrum, on top of the background features. Figures 5-7 shows the IR spectra of products formed following the generation of four different
alkoxy radicals: \( n \)-butoxy (Figure 5), 2-pentoxy (Figure 6), isobutoxy, and tert-butoxy (Figure 7). All radicals were produced from photolysis of the corresponding alkyl nitrites at 351 nm in the absence (Figures 5a and 6a) and presence (Figures 5b, 6b, 7) of \( O_2 \). Following photolysis of \( n \)-butyl nitrite and 2-pentyl nitrite, clear peaks are observed in the OH-stretch region, located at 3675 cm\(^{-1}\) (without \( O_2 \)) or 3676 cm\(^{-1}\) (with \( O_2 \)) for \( n \)-butyl nitrite, and 3658 cm\(^{-1}\) (without \( O_2 \)) or 3660 cm\(^{-1}\) (with \( O_2 \)) for 2-pentyl nitrite. These absorption features are broad (FWHM = 25 cm\(^{-1}\)), structureless, and asymmetric, with more intensity observed to the red of the peak. The general qualities of these peaks suggest that multiple conformers contribute to each observed absorption band. Furthermore, the observed peaks are similar in shape and position to the parent alcohols of the alkoxy radicals being studied. In the \( n \)-butoxy system (Figure 5), the observed absorption band is similar to the \( \nu_1 \) band of \( n \)-butanol (reference FTIR spectrum shown in green).\(^{77}\) Similarly, for the 2-pentoxy system (Figure 6), the observed absorption band is similar to the \( \nu_1 \) band of 2-pentanol.\(^{77}\) It should be noted that the absorption band is somewhat stronger and sharper in the presence of \( O_2 \) (Figures 5b and 6b) than in the absence of \( O_2 \) (Figure 5b). Analogous peaks were not observed following the photolysis of isobutyl nitrite or tert-butyl nitrite, as shown in Figure 7.

We assign the absorption bands presented in Figures 5 and 6 to the primary alkoxy isomerization products for the following reasons. First, the absorption bands that we observe are similar to the \( \nu_1 \) (OH stretch) bands of \( n \)-butanol and 2-pentanol. The primary isomerization products have structures similar to these alcohols (HOR• and HOROO• vs. ROH), and we expect similar infrared spectra. Second, we only observe the absorption features for alkoxy radicals that are long enough to undergo a 1,5-hydrogen shift (\( n \)-butoxy and 2-pentoxy). Neither isobutoxy nor tert-butoxy are long enough to isomerize, and thus any absorptions in the \( n \)-butoxy and 2-pentoxy systems that belonged to isomerization products would be missing. Finally, the arguments presented above in the Chemistry section indicate that the only significant products that we should be detecting under our experimental
conditions are the primary isomerization products. We therefore assign the IR spectra in Figures 5 and 6 to \( \delta\text{-HOC}_4\text{H}_8\text{•} \) (Figure 5a), \( \delta\text{-HOC}_4\text{H}_8\text{OO•} \) (Figure 5b), \( \delta\text{-HO-1-C}_3\text{H}_10\text{•} \) (Figure 6a), and \( \delta\text{-HO-1-C}_3\text{H}_10\text{OO•} \) (Figure 6b).

Table 2 summarizes the band positions and relative integrated intensities for \( \text{HOR•} \) and \( \text{HOROO•} \) for both the \( \text{n-butyl} \) and \( \text{2-pentyl} \) systems, and compares them to B3LYP/6-31+G(d,p) calculations. We note two key features of the \( \nu_1 \) spectra of \( \text{HOR•} \) and \( \text{HOROO•} \) presented in Figures 5 and 6 and Table 2. First, the position of the \( \nu_1 \) band slightly blue shifts upon addition of the peroxy group, by 1 cm\(^{-1}\) for the \( \text{n-butyl} \) system and 2 cm\(^{-1}\) for the \( \text{2-pentyl} \) system. Due to the large width of the \( \nu_1 \) peaks (FWHM = 25 cm\(^{-1}\)), it is difficult to determine whether this effect is statistically significant in our experimental spectra. Second, the band shape and integrated absorbance are affected by addition of the peroxy group. For both systems, the \( \text{HOROO•} \) spectra have a sharper \( \nu_1 \) peak than the \( \text{HOR•} \) spectra. The integrated absorbance of the \( \text{HOROO•} \) spectra is lower than the \( \text{HOR•} \) spectra; however, the addition of \( \text{O}_2 \) reduces the amount of isomerization product formed due to competition of the alkoxy isomerization and \( \text{O}_2 \) pathways. By accounting for this effect, we can calculate relative integrated intensities of the \( \nu_1 \) bands. We observe that the relative integrated intensities of \( \delta\text{-HOC}_4\text{H}_8\text{•} \) and \( \delta\text{-HOC}_4\text{H}_8\text{OO•} \) are equal within our experimental error (\( I_{\text{HOROO•}} / I_{\text{HOR•}} = 1.0 \)). However, addition of the peroxy group to the \( \text{2-pentoxy} \) system results in a significant increase in \( \nu_1 \) intensity (\( I_{\text{HOROO•}} / I_{\text{HOR•}} = 1.2 \)). The quantum chemistry calculations predict an increase in intensity upon addition of the peroxy group for both systems.

Furthermore, the intensity of \( \text{HOR•} \) is predicted to be similar to the parent alcohol, \( \text{ROH} \). We can therefore use the \( \text{HOR•} \) absorbance to estimate the initial concentration of alkoxy radicals, \( [\text{RO}]_0 \). Taking the absorption cross section of the \( \text{HOR•} \) \( \nu_1 \) peak to be equivalent to the parent alcohols (7.2 \( \times \) 10\(^{-20}\) molec cm\(^{-2}\) for \( \text{n-butanol} \), 6.0 \( \times \) 10\(^{-20}\) molec cm\(^{-2}\) for \( \text{2-pentanol} \)), \(^{77}\) we obtain \( [\text{HOC}_4\text{H}_8\text{•}]_0 = 1 \times 10^{14} \)
molec cm$^{-3}$ and $[\text{HOC}_3\text{H}_{10}\cdot]_0 = 5 \times 10^{13}$ molec cm$^{-3}$. These values are consistent with our estimate of the nascent alkoxy product yields (within a factor of 2).

**Photolysis of RONO at 248 nm vs. 351 nm and Assessment of Prompt Decomposition**

Figure 9 shows the IR spectra of products formed following the photolysis of $n$-butyl nitrite (Figure 9a) and 2-pentyl nitrite (Figure 9b), in the absence of O$_2$. In contrast to the spectra presented in Figures 5 and 6, the spectra in Figure 9 cover a larger frequency range, 3400-3700 cm$^{-1}$. Furthermore, $n$-butyl nitrite photolysis was performed at two UV wavelengths: 248 nm (laser fluence 125 mJ cm$^{-2}$) and 351 nm (laser fluence 150 mJ cm$^{-2}$). In addition to the $\nu_1$ peak of HOR•, we observe a second absorption near 3470 cm$^{-1}$ in these spectra. This feature is most pronounced following 248 nm photolysis (Figure 9a), although weaker absorptions can still be observed following 351 nm photolysis of both nitrites. The feature centered at 3470 cm$^{-1}$ following $n$-butyl nitrite photolysis (Figure 9a) matches the position and band shape of the $2\nu_2$ band of formaldehyde (HCHO), one of the products of unimolecular decomposition of $n$-butoxy (Reaction 6). It is likely that the analogous feature following 2-pentyl nitrite is the $2\nu_2$ band of acetaldehyde (CH$_3$CHO), one of the products of unimolecular decomposition of 2-pentoxy (Reaction 9a).

We can estimate the prompt decomposition yields of $n$-butoxy and 2-pentoxy following alkyl nitrite photolysis at 248 nm and 351 nm using the spectra in Figure 9. The absorption cross sections for HCHO (Q branch) and CH$_3$CHO (broad absorption) are known, and the quantum chemical calculations presented in the Spectra section suggest that the absorption cross section of HOR• is equivalent to the parent alcohol ROH. On the basis of these absorption cross sections and our spectra, we estimate prompt decomposition yields upon photolysis of the corresponding alkyl nitrite of 77% ± 14% (2σ) for $n$-butoxy at 248 nm, 11% for $n$-butoxy at 351 nm, and 26% for 2-pentoxy at 351 nm. It should be emphasized that these values should be considered upper limits for two reasons. First, the $2\nu_2$ signals in
the 351 nm photolysis experiments were only slightly stronger than the noise level of our spectrometer.

Second, additional HCHO or CH₃CHO could form through a prompt decomposition channel of the alkyl nitrite (reactions 23 and 24), contributing intensity to the 2ν₂ carbonyl band that is not due to prompt decomposition of the alkoxy radical itself.

\[ C_4H_9ONO^* \rightarrow C_3H_7^* + HCHO + NO \]  \( (23) \)

\[ C_3H_{11}ONO^* \rightarrow C_3H_7^* + CH_3CHO + NO \]  \( (24a) \)

\[ C_3H_{11}ONO^* \rightarrow CH_3^* + C_3H_7CHO + NO \]  \( (24b) \)

As will be shown in the Effect of Alternate Reaction Pathways section, the fraction of prompt decomposition does not affect our relative kinetics interpretation. However, a large amount of prompt decomposition has two undesirable effects. First, fewer alkoxy radicals are available for isomerization, reducing the OH stretch intensity being measured. Second, additional alkyl radicals are produced, introducing the possibility of unwanted secondary chemistry. In order to minimize the role of prompt decomposition, all kinetics data were analyzed from spectra taken using 351 nm as the photolysis wavelength.

**Time-Dependence of δ-HOC₄H₂OO⁻ Appearance**

In principle, we can determine the rate of n-butoxy isomerization by fitting the rise time of the δ-HOC₄H₂OO⁻ absorbance (3662 cm⁻¹) shown in Figure 8. However, the lifetime we obtain, on the order of 5 µs, is comparable to the empty-cell ringdown lifetime (7 µs), making it difficult to extract a reliable first order rate constant. Our data are consistent with the isomerization rate constant from previous studies, roughly 2 × 10⁵ s⁻¹. ¹⁵, ²⁶, ²⁸⁻³⁰, ³³, ³⁵

**Dependence of ν₁ Absorbance on [O₂] and Relative Kinetics Measurements**
While we cannot measure the kinetics of alkoxy isomerization directly from the time-resolved product appearance, we can obtain the isomerization rate from a relative rate measurement with respect to reaction with $O_2$. Since reaction with $O_2$ (reactions 4 and 7) competes with isomerization, as $[O_2]$ is increased, fewer alkoxy radicals isomerize (reactions 5 and 8), leading to a reduction in the $\nu_1$ absorbance of HOROO•. We can therefore determine the ratio of rate constants $k_{\text{isom}}/k_{O2}$ by measuring the relative change in $\nu_1$ absorbance as a function of $[O_2]$.

A key point in our approach is that we need measure only relative changes in absorbance, thus obviating the need to determine absolute concentrations. We can show that the ratio of absorbances gives us the ratio of the yields for isomerization (versus reaction with $O_2$). Define $A$ as the OH stretch absorbance for a given $[O_2]$, and $A_0$ as the OH stretch absorbance for $[O_2] = 0$ Torr. It will be shown later that $A_0$ is taken to be the intercept of a regression line rather than the literal absorbance at $[O_2] = 0$ Torr, because HOR• and HOROO• have different $\nu_1$ bands, as shown in the Spectra section above. By Beer’s Law, the ratio of $A_0$ to $A$ in the weak absorbance limit is

$$\frac{A_0}{A} = \frac{\sigma_{\text{HOROO•}} L_{\text{phot}} ([\text{HOROO•}]_{[O_2]=0})}{\sigma_{\text{HOROO•}} L_{\text{phot}} [\text{HOROO•}]} = \frac{([\text{HOROO•}]_{[O_2]=0})}{[\text{HOROO•}]},$$

(25a)

where $\sigma_{\text{HOROO•}}$ is the $\nu_1$ cross section of HOROO• and $L_{\text{phot}}$ is the photolysis length (sample length of HOROO•). Furthermore, we can convert $[\text{HOROO•}]$ to an isomerization yield $\phi_{\text{isom}}$ by equation 25b:

$$\frac{A_0}{A} \frac{([\text{HOROO•}]_{[O_2]=0})}{[\text{HOROO•}]} = \frac{([\text{HOROO•}]_{[O_2]=0})}{[\text{HOROO•}]}$$

(25b),

assuming that $[RO•]_0$, the initial concentration of alkoxy radicals that can undergo isomerization, is the same in the two experiments.

If we assume simplistically that the alkoxy radicals can undergo only thermal isomerization or reaction with $O_2$, then one can show that
Absorbance data were collected by one of two methods. In the first method, \( \nu_1 \) spectra were recorded at various \([O_2]\) with a larger step size (0.5 cm\(^{-1}\) instead of 0.2 cm\(^{-1}\)) than presented in the Spectra section. In the second method, absorbance data were collected at a single frequency at times after photolysis where the \( \nu_1 \) absorbance had reached its maximum value (20-120 \( \mu s \)). We verified that our relative absorbance data were insensitive to the choice of method, as expected from the invariance in \( \nu_1 \) peak shape with respect to \([O_2]\) shown in Figure 11. Data were taken in sets of 7 – 10 different \([O_2]\) across the range \((0 – 1.7) \times 10^{19} \text{ molec cm}^{-3}\). Each set of absorbance data was fit separately to a line, and the y-intercept was taken to be \( A_0 \). This procedure of collecting data in sets minimizes the impact of long-term drifts in precursor concentrations or laser fluences upon our absorbance measurements.

Plots of \( A_0/A \) vs. \([O_2]\) for \( n \)-butoxy and 2-pentoxy taken at 670 Torr are shown in Figures 10a and 10b. For \([O_2] > 10^{17} \text{ molec cm}^{-3}\), the \( \nu_1 \) absorbance decreases with increasing \([O_2]\), consistent with the competition of the isomerization and \( O_2 \) reaction pathways. The data are roughly linear. For very low oxygen concentrations \(([O_2] < 3 \times 10^{16} \text{ molec cm}^{-3})\), we observe an increase in absorbance with increasing \([O_2]\), shown in red on Figure 10a and expanded in Figure 11. This effect is likely attributable to the change in product being detected as \([O_2]\) is increased. At \([O_2] = 0 \text{ Torr}\), only the immediate isomerization product \( \text{HOR}^\bullet \) forms (reaction 15). As \( O_2 \) is added to the system, the isomerization product changes to \( \text{HOROO}^\bullet \) (reaction 20). Differences in \( \nu_1 \) peak absorption cross sections between \( \text{HOR}^\bullet \) and \( \text{HOROO}^\bullet \) likely cause the non-linearity observed at low \([O_2]\), where not all \( \text{HOR}^\bullet \) will have converted to peroxy radicals in 20 \( \mu s \). Despite the apparent decrease of \( A_0/A \) at low \([O_2]\), an accurate value of \( k_{\text{isom}}/k_{O_2} \) should be obtained when \([O_2]\) is high enough to ensure rapid conversion of \( \text{HOR}^\bullet \) to \( \text{HOROO}^\bullet \). As a result, only data with \([O_2] > 10^{17} \text{ molec cm}^{-3}\) were used to determine \( k_{\text{isom}}/k_{O_2} \).
Several data sets were taken replacing all \( \text{N}_2 \) with Ar to observe the impact of the collision partner. The Ar data sets resulted in values of \( k_{\text{isom}}/k_{\text{O}_2} \) that were statistically identical to the \( \text{N}_2 \) data, indicating that 670 Torr lies near the high-pressure limit of the termolecular falloff curve, in agreement with RRKM calculations.\(^{23} \)

**Effect of Alternate Reaction Pathways of RO•: Prompt Isomerization, Decomposition, and Recombination with NO**

We next consider the effect of minor channels, and in particular prompt isomerization of hot alkoxy radicals and reaction with background NO (primarily from RONO photolysis), on the apparent isomerization yield, and analyze the alkoxy kinetics to determine the isomerization yield \( \phi_{\text{isom}} \) from the observed relative absorbance measurements.

Photolysis of the alkyl nitrite yields thermalized alkoxy (RO•) and NO (reaction 14), or hot alkoxy (RO•\(^*\)) and hot NO\(^*\) (reaction 27). Thermalized alkoxy radicals can undergo one of four reactions in our experiment: isomerization followed by association with \( \text{O}_2 \) (reactions 15 and 20), reaction with \( \text{O}_2 \) (reaction 28), decomposition (reaction 29), or recombination with NO (reaction 30). Hot alkoxy radicals can undergo one of two reactions: prompt isomerization (reaction 12) or prompt decomposition (reaction 13).

\[
\begin{align*}
\text{RONO} \rightarrow^{h\nu} \text{RO}^\bullet + \text{NO} & \quad (14) \\
\text{RONO} \rightarrow^{h\nu} \text{RO}^\bullet + \text{NO}^* & \quad (27) \\
\text{RO}^\bullet \rightarrow \text{HOR}^\bullet & \quad (15) \\
\text{HOR}^\bullet + \text{O}_2 \rightarrow \text{HOROO}^* & \quad (20) \\
\text{RO}^\bullet + \text{O}_2 \rightarrow \text{RCHO} + \text{HO}_2 & \quad (28) \\
\text{RO}^\bullet \rightarrow \text{R}^\bullet + \text{R}^\bullet \text{CHO} & \quad (29)
\end{align*}
\]
RO• + NO• → RONO  \tag{30}

\textit{prompt} \quad \text{RO•} \quad \text{HOR•}  \tag{12}

\textit{prompt} \quad \text{RO•} \rightarrow R'• + R''CHO  \tag{13}

The fraction of alkoxy prompt decomposition (reaction 13) does not affect our relative kinetics measurements, because prompt decomposition simply reduces the initial number of alkoxy radicals available. The fraction of alkoxy radicals formed from photolysis of the alkyl nitrite (reactions 14 and 25) can be written as

\[ [\text{RO•}]_{\text{from photolysis}} = [\text{RONO}] F_{UV} \sigma_{UV} \]

where \( F_{UV} \) is the flux of light (photons cm\(^{-2}\)) from the photolysis (excimer) laser through the CRDS cell. Define \( \phi_{pd} \) as the fraction of alkoxy radicals that undergo prompt decomposition. Then the alkoxy radicals left over that can undergo all other reactions can be written as

\[ [\text{RO•}]_0 = [\text{RO•}]_{\text{from photolysis}} (1 - \phi_{pd}) = [\text{RONO}] F_{UV} \sigma_{UV} (1 - \phi_{pd}) \]

The terms \( \sigma_{UV} \) and \( \phi_{pd} \) are constant for a given UV wavelength. These terms can be combined into a single “effective UV cross section” \( \sigma_{UV,eff} \):

\[ \sigma_{UV,eff} = \sigma_{UV} (1 - \phi_{pd}) \]

Substituting equation 33 into equation 32 yields

\[ [\text{RO•}]_0 = [\text{RONO}] F_{UV} \sigma_{UV,eff} \]

The result is that prompt decomposition can be accounted for in the initial photolysis step, and does not need to be included in the relative kinetics analysis.

Although prompt decomposition does not affect the relative rate measurements, the remaining five pathways still contribute to the experiment. We therefore define \( \phi_{isom} \) in equation 26 as the fraction
of alkoxy radicals that do isomerize, but did not promptly decompose. The two sources of HOROO• are prompt isomerization (reaction 12) and regular isomerization (reaction 15). \( \phi_{isom} \) can be written as

\[
\phi_{isom} = \phi_{pi} + (1 - \phi_{pi}) \frac{k_{isom}}{k_{isom} + k_{O_2} [O_2] + k_{decomp} + k_{NO} [NO]} \tag{35}
\]

where \( \phi_{pi} \) is the prompt isomerization yield, and \( k_{isom}, k_{O_2}, k_{decomp}, \) and \( k_{NO} \) are the rate constants for reactions 15, 28, 29, and 30 respectively. Substituting equation 35 into equation 26 gives the following relationship between absorbance and \([O_2]\):

\[
\frac{A_0}{A} = \frac{\left( \frac{k_{O_2}}{k_{isom}} \right) [O_2] + 1}{1 + \left( \frac{k_{decomp}}{k_{isom}} + \frac{k_{NO} [NO]}{k_{isom}} \right) \left( \frac{\phi_{pi} k_{O_2}}{k_{isom}} \right) \left( \frac{k_{decomp}}{k_{isom}} + \frac{k_{NO} [NO]}{k_{isom}} \right) [O_2] + 1} \tag{36}
\]

According to equation 36, we can still analyze a plot of \( A_0/A \) vs. \([O_2]\) to obtain the relative rate \( k_{isom}/k_{O_2} \). Similar to the simplistic analysis presented initially (equation 26), our measurements are still independent of absolute alkoxy concentrations, absolute n1 absorbances, or absolute absorption cross sections; only the absorbance relative to the absorbance at \([O_2] = 0 \) Torr is required.

In the absence of significant prompt isomerization, or at low \([O_2]\), the denominator of equation 36 reduces to 1. In these limiting cases, equation 36 reduces to

\[
\lim_{\phi_{pi} \to 0} \frac{A_0}{A} = \lim_{[O_2] \to 0} \frac{A_0}{A} = \frac{k_{O_2}}{k_{isom} + k_{decomp} + k_{NO} [NO]} [O_2] + 1 \tag{37}
\]

When equation 37 holds true, \( A_0/A \) depends linearly on \([O_2]\). This linear relation indicates that \( A_0 \) can still be obtained through linear regression when accounting for the effects of minor reaction channels.
Correction Factors for $k_{\text{isom}}/k_{O_2}$

The typical analysis of alkoxy relative kinetics found in the literature assumes that the only important alkoxy reactions are isomerization and reaction with $O_2$; i.e., $k_{\text{decomp}}$, $k_{\text{NO}}$, and $\phi_{\text{pi}}$ are negligible. In this limit, equation 36 reduces to equation 26 and the relative rate $k_{\text{isom}}/k_{O_2}$ would be obtained from absorbance data by equation 38:

$$
\frac{k_{\text{isom}}}{k_{O_2}} = \left[ \frac{\partial \left( \frac{A_0}{A} \right)}{\partial \left[ O_2 \right]} \right]^{-1} \tag{38}
$$

Taking the analogous derivative using equation 36 in the limit of low $[O_2]$, where the plot of $A_0/A$ vs. $[O_2]$ is linear, and solving for $k_{\text{isom}}/k_{O_2}$, gives

$$
\frac{k_{\text{isom}}}{k_{O_2}} = \left[ \frac{\partial \left( \frac{A_0}{A} \right)}{\partial \left[ O_2 \right]} \right]^{-1} \left[ \frac{1}{1 + \frac{k_{\text{decomp}}}{k_{\text{isom}}} + \frac{k_{\text{NO}}[\text{NO}]}{k_{\text{isom}}}} \right] \left[ \frac{1 - \phi_{\text{pi}}}{1 + \phi_{\text{pi}} \left( \frac{k_{\text{decomp}}}{k_{\text{isom}}} + \frac{k_{\text{NO}}[\text{NO}]}{k_{\text{isom}}} \right)} \right] \tag{39}
$$

The first term in equation 39 represents the $k_{\text{isom}}/k_{O_2}$ that would have been calculated if prompt isomerization, decomposition, and reaction with NO were ignored. The second term represents a "correction factor" to account for the two kinetic alkoxy pathways: decomposition and reaction with NO. The third term is a "correction factor" to account for prompt isomerization. Define these correction factors as $X_{\text{kin}}$ and $X_{\text{prompt}}$, where

$$
X_{\text{kin}} = \frac{1}{1 + \frac{k_{\text{decomp}}}{k_{\text{isom}}} + \frac{k_{\text{NO}}[\text{NO}]}{k_{\text{isom}}}} \tag{40}
$$

$$
X_{\text{prompt}} = \frac{1 - \phi_{\text{pi}}}{1 + \phi_{\text{pi}} \left( \frac{k_{\text{decomp}}}{k_{\text{isom}}} + \frac{k_{\text{NO}}[\text{NO}]}{k_{\text{isom}}} \right)} \tag{41}
$$
This allows us to rewrite equation 39 in a simpler form

\[
\frac{k_{\text{isom}}}{k_{\text{O}_2}} = \left[ \frac{\partial \left( \frac{A_0}{A} \right)}{\partial [\text{O}_2]} \right]^{-1} \times X_{\text{kin}} \times X_{\text{prompt}}
\]  \tag{42}

Table 3 summarizes the parameters used for calculating \(k_{\text{isom}}/k_{\text{O}_2}\). \(\left( \frac{\partial \left( \frac{A_0}{A} \right)}{\partial [\text{O}_2]} \right)\) was calculated by performing linear regression to our absorbance data. The 2\(\sigma\) error includes both error on the slope and intercept of the regression line. \(k_{\text{decomp}}\) and \(k_{\text{NO}}\) were taken from the literature \cite{26, 72} and estimated to have 50\% uncertainty. \(k_{\text{isom}}\) was estimated as

\[
\left( \frac{\partial \left( \frac{A_0}{A} \right)}{\partial [\text{O}_2]} \right) \times [\text{NO}]\]

was taken to be equal to the [RO] used (2 \(\times\) 10\(^{14}\) molec cm\(^{-3}\)). \(\phi_{\text{pi}}\) was calculated by a numerical nonlinear least squares analysis (0.04 ± 0.02 for \(n\) -butoxy, 0.05 ± 0.02 for 2-pentoxy). Significant amounts of prompt isomerization would lead to non-linearity in the plot of \(A_0/A\) vs. [\(\text{O}_2\)]. Figure 10 shows fits of equation 36 to our absorbance data for the value of \(\phi_{\text{pi}}\) found from our non-linear least squares analysis, \(\phi_{\text{pi}} = 0\), and \(\phi_{\text{pi}} = 0.20\). The plots show that our data are described well for the values of \(\phi_{\text{pi}}\) obtained from our least squares analysis, but are described poorly for large amounts of prompt isomerization.

Using the rate constants and parameters in Table 3, the overall correction factor \(X_{\text{kin}} \times X_{\text{prompt}}\) is

0.93 ± 0.03 for \(n\) -butoxy and 0.87 ± 0.04 for 2-pentoxy.

**Determination of \(k_{\text{isom}}/k_{\text{O}_2}\)**

The analysis above allows us to obtain the ratio of the rate constants for isomerization versus reaction with \(\text{O}_2\) for each of the two alkoxy radicals: \(k_{\text{isom}}/k_{\text{O}_2} = (1.69 ± 0.15) \times 10^{19}\) cm\(^{-3}\) for \(n\) -butoxy, and
(3.37 ± 0.43) × 10^{19} \text{ cm}^{-3} for 2-pentoxy (See Table 3). These results take into account the small but
significant curvature in the dependence of $A_0/A$ on $O_2$ pressure arising from (1) prompt isomerization of
hot alkoxy radicals, (2) unimolecular alkoxy decomposition, and (3) recombination with background NO.

DISCUSSION

Comparison to previous measurements

Our values for $k_{\text{isom}}/k_{O_2}$ are compared with previous measurements in Table 4. For both $n$-butoxy
($k_{\text{isom}}/k_{O_2} = 1.69 \pm 0.15 \times 10^{19} \text{ cm}^{-3}$) and 2-pentoxy ($k_{\text{isom}}/k_{O_2} = 3.37 \pm 0.43 \times 10^{19} \text{ cm}^{-3}$), our measured
$k_{\text{isom}}/k_{O_2}$ are consistent with the values reported in the literature and with reduced uncertainty by a
factor of 2-3 (9% and 13% uncertainty respectively, 2σ). Previous experimental studies of the $n$-butoxy
radical at 1 atm have obtained values for $k_{\text{isom}}/k_{O_2}$ ranging from $1.5 \times 10^{19}$ to $2.1 \times 10^{19}$ \text{ cm}^{-3}.^{15, 28-30, 33, 35}$

The IUPAC data evaluation reports a preferred value of $(2.1 \pm 1.8) \times 10^{19}$ for $k_{\text{isom}}/k_{O_2}$ at 298 K and 1 bar
pressure, assuming $k_{O_2}$ of $(1.4 \pm 1.0) \times 10^{14} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}.^{11}$ The majority of these studies$^{15, 26, 28, 30, 33, 35}$
relied on detection of $n$-butanal (the product of alkoxy reaction with $O_2$) with no detection of the
isomerization pathway. Cassanelli et al. $^{29}$ quantify the isomerization pathway by measuring 4-hydroxy
butanal, a secondary product generated from further reaction of $\delta$-HO-C$_5$H$_9$OO•. These secondary
product analyses are in good agreement with our measured $k_{\text{isom}}/k_{O_2}$ for $n$-butoxy of $(1.69 \pm 0.15) \times 10^{19}$
\text{ cm}^{-3} via direct detection of the isomerization product. This suggests that the secondary chemistry used
in previous studies is well modeled, or that the errors in each secondary step cancel each other out. The
results of the fast flow study by Hein, $^{33}$ which measured NO in real time, were performed at lower
pressures (38 Torr) and cannot be compared directly to our results. Similarly, our measured $k_{\text{isom}}/k_{O_2}$ for
2-pentoxy of $(3.37 \pm 0.43) \times 10^{19}$ \text{ cm}^{-3} is in good agreement with Atkinson’s previous measurements $(3.1$
\times 10^{19} \text{ cm}^{-3}, factor of 2 uncertainty).$^{12}$ Both our and Atkinson’s $k_{\text{isom}}/k_{O_2}$ disagree with Dóbé’s result by a
factor of 20 ($k_{\text{isom}}/k_{O_2} = 0.15 \times 10^{19} \text{ cm}^{-3}$).$^{31}$ Dóbé’s study used methyl radicals to convert the $\delta$-HO-1-
C₅H₁₀• to 2-hexanol, and it is possible that additional secondary chemistry could significantly alter their results.

While there is good agreement between our $k_{\text{isom}}/k_{O2}$ values with the existing literature values, it should be noted that previous studies did not consider how additional alkoxy reactions (decomposition, recombination with NO, prompt isomerization) would affect the calculated value of $k_{\text{isom}}/k_{O2}$. In our experiment, the difference between including and ignoring these three reactions is a factor of $X_{\text{kin}} \times X_{\text{prompt}} (0.93 \pm 0.03$ for $n$-butoxy and $0.87 \pm 0.04$ for 2-pentoxy). Ignoring these corrections will cause a systematic overestimation of $k_{\text{isom}}/k_{O2}$ (7% reduction for $n$-butoxy, 13% for 2-pentoxy). It may be necessary to apply similar correction factors to the previous alkoxy relative kinetics experiments. For example, some of the previous $n$-butoxy experiments made use of elevated [NO], as high as $9 \times 10^{14}$ molec cm$^{-3}$ in order to drive secondary chemistry to completion. For this [NO], the relative rate of reaction with NO to isomerization is $\frac{k_{NO} [NO]}{k_{\text{isom}}} = 0.12$, roughly equal to the 1σ uncertainties on the previously reported $k_{\text{isom}}/k_{O2}$ values. It would be worthwhile to determine whether the previously reported $k_{\text{isom}}/k_{O2}$ values for $n$-butoxy require revision in light of the correction factors presented in equations 40-42.

Contributions to and Sensitivity of Correction Factors

The parameters in Table 3 show that the major contributions to the correction factors are different for $n$-butoxy and 2-pentoxy. For $n$-butoxy, $X_{\text{kin}}$ and $X_{\text{prompt}}$ are roughly equal (0.97 and 0.96 respectively). The major contribution to $X_{\text{kin}}$ is recombination with NO ($\frac{k_{NO} [NO]}{k_{\text{isom}}} = 0.026$), while the effects of decomposition are negligible ($\frac{k_{\text{decomp}}}{k_{\text{isom}}} = 0.002$). In contrast, for 2-pentoxy, $X_{\text{kin}}$ is a more significant correction than $X_{\text{prompt}}$ (0.92 compared to 0.95). Decomposition is the major contributor to $X_{\text{kin}}$.
\( \frac{k_{\text{decomp}}}{k_{\text{isom}}} = 0.065 \), although recombination with NO still remains significant \( \frac{k_{\text{NO}}[\text{NO}]}{k_{\text{isom}}} = 0.022 \). The reported correction factors and contributions are valid for our experimental conditions, \([\text{NO}] = 2 \times 10^{14} \text{molec cm}^{-3}\); changing \([\text{NO}]\) will change the importance of the NO recombination reaction on the relative kinetics analysis.

Given that the parameters \(k_{\text{decomp}}, k_{\text{NO}} \times [\text{NO}],\) and \(k_{\text{isom}}\) are subject to somewhat large uncertainties, and that different alkoxy studies have made use of different \([\text{NO}]\), it is useful to determine how sensitive \(X_{\text{kin}}, X_{\text{prompt}},\) and the total correction factor are to each parameter. Table 5 contains the partial derivatives of the correction factors with respect to the parameters \(k_{\text{decomp}}/k_{\text{isom}}, k_{\text{NO}} \times [\text{NO}]/k_{\text{isom}},\) and \(\phi_p\). The derivatives are reported at the values of \(k_{\text{decomp}}/k_{\text{isom}}, k_{\text{NO}} \times [\text{NO}]/k_{\text{isom}},\) and \(\phi_p\) used to calculate the correction factors (in Table 3). For both systems, the derivative of \(X_{\text{kin}} \times X_{\text{prompt}}\) with respect to \(k_{\text{decomp}}/k_{\text{isom}}\) and \(k_{\text{NO}} \times [\text{NO}]/k_{\text{isom}},\) and \(\phi_p\) used to calculate the correction factors (in Table 3). For both systems, the derivative of \(X_{\text{kin}} \times X_{\text{prompt}}\) with respect to \(\phi_p\) is the same (-1.00).

The fact that \(\frac{\partial \left( X_{\text{kin}} \times X_{\text{prompt}} \right)}{\partial \left( \frac{k_{\text{NO}}[\text{NO}]}{k_{\text{isom}}} \right)}\) is large for both systems underscores the need to analyze each previous experiment separately if correction factors need to be applied. Across a range of \([\text{NO}]\) of \((1 – 9) \times 10^{14} \text{molec cm}^{-3}\), \(X_{\text{kin}} \times X_{\text{prompt}}\) would change by -0.10 for \(n\)-butoxy (from 0.95 to 0.85) and -0.07 for 2-pentoxy (from 0.88 to 0.81). Furthermore, \(k_{\text{decomp}}\) for 2-pentoxy is relatively large, and its uncertainty is large due to the relative lack of experimental studies on 2-pentoxy decomposition. Across a range of \(k_{\text{decomp}}\) of \((1 – 2) \times 10^{4} \text{s}^{-1}\), \(X_{\text{kin}} \times X_{\text{prompt}}\) will change by -0.03 (from 0.90 to 0.87). (The rate of decomposition for \(n\)-butoxy, 600 \text{s}^{-1}, is too small for the exact value of \(k_{\text{decomp}}\) to have any appreciable effect on the correction factor). Determining \(k_{\text{decomp}}\) for 2-pentoxy to higher precision than currently available will help reduce the uncertainty on its relative kinetics measurements.
Prompt Decomposition and Prompt Isomerization

There have been a number of studies of alkyl nitrite photolysis, including several recent papers on n-butyl nitrite photolysis. However, only the paper by Bruhlmann et al. on methyl nitrite photodissociation provides estimates of the partitioning of available energy into product translation, vibration, and rotation (at 363 nm). There is some discrepancy however, with results by Schwartz-Lavi et al. on tert-butyl nitrite, in which the NO is found to have approximately 20% of available energy in NO rotation rather than 3%. However, if we assume from the methyl nitrite results that 20% of the available energy is in alkoxy internal energy, with the majority in vibration, then ≈8 kcal mol⁻¹ is internal energy in RO statistically distributed among 36 degrees of freedom, and we expect the initial vibrational temperature to be approximately 400 K. There will be competition between isomerization of the hot radical and collisional quenching. If we assume <ΔE> = 100 cm⁻¹ / collision and gas kinetic collision rate, then collisional quenching should occur in less than 100 ns, suggesting that most of the hot radicals would collisionally relax. The observed prompt isomerization yield of <5% is consistent with this qualitative picture.

In the atmosphere, the alkoxy radicals are formed from the reaction of RO₂ and NO. This reaction for n-butoxy is exothermic by 10 kcal mol⁻¹. While the products may be formed chemically activated, at 1 atm, we expect that similar competition between quenching and isomerization to take place if hot radicals are formed.

We have also investigated the possibility of prompt decomposition and isomerization of the alkoxy radical. When high energy radiation (248 nm) was used for photolysis of n-butyl nitrite, we observed significant quantities of the decomposition product formaldehyde. We place an upper limit of 77% for the prompt decomposition channel of n-butoxy following photolysis of n-butyl nitrite at 248 nm. In contrast, little to no formaldehyde was detected when photolysis of n-butyl nitrite was initiated with 351 nm radiation. A small amount of acetaldehyde was observed following photolysis of 2-pentyl nitrite.
at 351 nm. We place upper limits on the prompt decomposition pathways of 11% for \(n\)-butoxy and 26% for 2-pentoxy following photolysis of the alkyl nitrite at 351 nm. The enthalpy of breaking the O-NO bond in \(n\)-butyl nitrite is 42 kcal mol\(^{-1}\).\(^6\) In our experiments, the excimer supplies 115 kcal mol\(^{-1}\) (248 nm) or 81 kcal mol\(^{-1}\) (351 nm). Thus, the excess energy present in the \(n\)-butoxy and NO fragments after photolysis is 73 kcal mol\(^{-1}\) (248 nm) or 39 kcal mol\(^{-1}\) (351 nm). For \(n\)-butoxy, the barrier to decomposition is 15 kcal mol\(^{-1}\).\(^5\) At 248 nm, enough excess energy is stored in the \(n\)-butoxy fragment to go through non-thermal decomposition. The significantly weaker formaldehyde signal during 351 nm photolysis suggests that most of the excess 39 kcal mol\(^{-1}\) is distributed to the NO fragment, internal vibrational and torsional modes of \(n\)-butoxy, and translational modes of both fragments.

Isomerization has a barrier of 10 kcal mol\(^{-1}\),\(^5\) which is lower than the barrier to decomposition, but it must proceed through a tight transition state. It is expected that for 248 nm photolysis, some of the alkoxy radicals will undergo significant amounts of prompt isomerization. This has been modeled by Mereau \textit{et al.}, and Vereecken and Peeters.\(^{24,84}\) We did not measure \(k_{\text{isom}}/k_{\text{O2}}\) using 248 nm light to photolyze the alkyl nitrites, and thus cannot directly compare prompt isomerization in our experiment to Geiger \textit{et al.}\(^{34}\) Our measurements of \(n\)-butoxy decomposition do support Geiger’s observation that formation of hot radicals is important for photolysis at 254 nm. We can, however, compare our prompt isomerization analysis (351 nm photolysis) to Cassanelli \textit{et al.}’s work (370±10 nm photolysis).\(^{29}\) We calculate a prompt isomerization yield of 4% for \(n\)-butoxy and 5% for 2-pentoxy. This is in reasonable agreement with Cassanelli \textit{et al.}’s estimate of \(\sim 10\%\) ‘hot’ alkoxy radicals from their photolysis of 2-butynitrite/NO/N\(_2\)/O\(_2\).

\textbf{Internal Hydrogen Bonding of \(\delta\text{-HOC}_2\text{H}_3\text{OO}^+\)}

Internal hydrogen bonding can lead to complexity in the vibrational spectra of a molecule. Recent spectra and computations on peroxynitrous acid illustrate this phenomenon.\(^{36,37,85-97}\) Hydrogen
bonding will cause a red shift in the OH stretch frequency, affecting the measured $\nu_1$ intensities in our spectra. It is therefore important to estimate how much HOC$_4$H$_8$OO• hydrogen bound. We can construct a simple model to make our estimate by comparing a hydrogen bound conformer (8-membered ring) to the linear conformer of HOC$_4$H$_8$OO•. It can be shown that the percentage of HOROO• that is hydrogen bound is given by

$$% \text{HOROO H-bonded} = \frac{f \times \left( \frac{q_{trs}q_{rot}q_{vib}q_{el}}{q_{trs}q_{rot}q_{vib}q_{el}} \right)_{\text{H-bond}} \times \exp \left[ -\frac{D_0}{kT} \right]}{(1 - f) + f \times \left( \frac{q_{trs}q_{rot}q_{vib}q_{el}}{q_{trs}q_{rot}q_{vib}q_{el}} \right)_{\text{non-H-bond}} \times \exp \left[ -\frac{D_0}{kT} \right]}$$

(43),

where $f$ is the fraction of total HOROO• conformers that are hydrogen bound, $q_i$ are the partition functions, and $D_0$ is the energy difference between the hydrogen bound conformer and the linear conformer. We estimate $f$ to be 1/6, based on analysis of the $3^5 = 243$ conformers of HOC$_4$H$_8$OO• (as a function of the 5 dihedral angles HO1C1C2, OC1C2C3, C1C2C3C4, C2C3C4O2, C3C4O2O3). Not all conformers will contribute equally to hydrogen bonding; therefore, we present results for a range of $f$.

The $q_i$ were calculated at the B3LYP/6-31+G(d,p) level of theory and basis, using anharmonic frequencies in the calculation of $q_{vib}$. Based on this calculation, $\frac{\left( q_{trs}q_{rot}q_{vib}q_{el} \right)_{\text{H-bond}}}{\left( q_{trs}q_{rot}q_{vib}q_{el} \right)_{\text{non-H-bond}}} = 9.5 \times 10^{-2}$.

Based on our calculations, $D_0 = -160 \text{ cm}^{-1}$ (electronic energy difference). However, the hydrogen bond between methylperoxy and methanol is much stronger, $D_0 = -1450 \text{ cm}^{-1}$ (electronic energy difference). One possible reason for this discrepancy is ring strain of the 8 membered hydrogen bound conformer of HOROO•. (Calculations of 7-membered hydrogen bonded conformers yielded higher energies, and consequently a positive value of $D_0$). Since more negative values of $D_0$ will increase the percentage of HOROO• that is hydrogen bound, we present a range of results based on reasonable $D_0$ values.
Table 6 shows the percentage of HOROO• that is hydrogen bound as a function of the fraction of hydrogen bound conformers (f) and the hydrogen bond energy (D₀), on the basis of our simple model. At our calculated values of f = 0.16 and D₀ = -160 cm⁻¹, only 4% of the HOROO• will be hydrogen bound. This value is consistent with our observation that the observed ν₁ peak intensity of HOROO agrees with our estimate based on [RONO] and the photolysis flux. Furthermore, we observe that for f = 0.16 and D₀ values typical of CH₃OO-CH₃OH, D₀ = -1000 cm⁻¹ or -1500 cm⁻¹, a very significant fraction of HOROO would be hydrogen bound (69% or 95%). If such a large fraction of HOROO were hydrogen bound, we would observe very significant sequence band formation to the red of the main ν₁ peak, approximately 3550-3650 cm⁻¹.

CONCLUSIONS

We have reported the direct spectroscopic detection of the isomerization products of the n-butoxy and 2-pentoxy radicals, in the absence and presence of oxygen. The ν₁ (OH stretch) spectra of these species (δ-HOC₃H₈•, δ-HOC₃H₈OO•, δ-HO-1-C₅H₁₀•, and δ-HO-1-C₅H₁₀OO•) are similar in position and shape to the parent alcohols (n-butanol and 2-pentanol). The ν₁ bands of δ-HOC₃H₈•, δ-HOC₃H₈OO• are centered at 3675 cm⁻¹ and 3676 cm⁻¹ respectively, while the ν₁ bands of δ-HO-1-C₅H₁₀•, and δ-HO-1-C₅H₁₀OO• are centered at 3658 cm⁻¹ and 3660 cm⁻¹ respectively. The integrated intensity and peak shapes of the n₁ band differs slightly between HOR• and HOROO•. Observations of formaldehyde and acetaldehyde indicate significant prompt decomposition following photolysis of the alkyl nitrites at 248 nm and less significant prompt decomposition at 351 nm. The ν₁ spectra were used to determine the rate constant of isomerization relative to reaction with O₂. We find that for n-butoxy, k_isom/k_O₂ = (1.69 ± 0.15) × 10¹⁹ cm⁻³, while for 2-pentoxy, k_isom/k_O₂ = (3.37 ± 0.43) × 10¹⁹ cm⁻³. The uncertainties take into account the possible prompt isomerization of hot nascent RO• formed from RONO photolysis at 351 nm. Our experiments directly measure the concentration of the initial isomerization radical product within
microseconds after its formation, and do not rely on detailed knowledge of the secondary chemistry. Our relative kinetics analysis shows that commonly neglected alkoxy reactions (decomposition, recombination with NO, and prompt isomerization) have a significant effect on the interpretation of relative kinetics data. Under our experimental conditions, neglect of these reactions would have caused a 7% \((n\text{-butoxy})\) or 13% (2-pentoxy) overestimation of \(k_{\text{isom}}/k_{\text{O}_2}\).

We can estimate the ambient temperature isomerization rates from our relative rate measurements in Table 4 using the recommended rate constants for reaction with of \(\text{O}_2\). For \(n\text{-butoxy}\), we find \(k_{\text{isom}} = (2.37 \pm 1.2) \times 10^5 \text{ s}^{-1}\), assuming a rate coefficient of \(k_{\text{O}_2} = (1.4 \pm 0.7) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}\). For 2-pentoxy, we find an isomerization rate of \(2.70 \times 10^5 \text{ s}^{-1}\), assuming a rate coefficient of \(k_{\text{O}_2} = 8.0 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}\) (uncertainty not reported on this value). The isomerization rate at 670 Torr is predicted to be well above the high pressure limit and is thus likely to be identical to the rate at atmospheric pressure. The largest uncertainty in the absolute isomerization rate is in the estimate of the rate coefficient for reaction of the alkoxy radical with \(\text{O}_2\). However, we expect that by lowering the temperature to 273K, we will slow isomerization to rates within the resolution of the CRDS method, allowing us to measure the isomerization in real time.

ACKNOWLEDGEMENTS

Financial support was provided by the NASA Upper Atmosphere Research Program Grants NAG5-11657, NNG06GD88G, and NNX09AE21G; and the California Air Resources Board Contracts 03-333 and 07-730. Part of this research was carried out at the Jet Propulsion Laboratory, California Institute of Technology under contract to the National Aeronautics and Space Administration. MKS thanks the Department of Defense NDSEG Graduate Fellowship for funding. ERG was supported by an EPA STAR Graduate Research Fellowship. Support from the NASA UARP and Tropospheric Chemistry Program is acknowledged. AKM thanks the NASA Earth System Science and NSF Graduate Research.
Fellowship programs. MLW thanks the Caltech Student-Faculty Programs office for funding through the Summer Undergraduate Research Fellowship program. We thank Todd Fuelberth and Dave Natzic for building the OPA crystal rotation mechanism and other technical assistance, David Robichaud for LabVIEW programming, Ralph Page for optimization of the spectrometer optics, Nathan Eddingsaas for assistance with FTIR analysis of the 2-pentyl nitrite, Michael Roy for machining of the CRDS mirror mounts, and Richard Gerhart for glassware construction and repair.

APPENDIX

Thermodynamics of our 2-Pentyl Nitrite sample

To the best of our knowledge, the enthalpy of vaporization ($\Delta H_{vap}$), boiling point at atmospheric pressure ($T_{boil}$), and the vapor pressure as a function of temperature ($p_{vap}(T)$) of 2-pentyl nitrite have not been reported in the chemical literature. In this appendix, we report the vapor pressure measurements of our 2-pentyl nitrite sample and our derivation of the thermodynamic parameters $\Delta H_{vap}$ and $T_{boil}$.

Our experimental apparatus is shown in Figure A1. A 3-necked round-bottomed flask containing 50 mL of 2-pentyl nitrite was immersed in a water bath. The three necks of the flask were fit to a thermometer, two pressure gauges (MKS Baratron and Duniway thermocouple gauge), and an air / vacuum line to control pressure. Data were obtained by cooling the 2-pentyl nitrite sample, removing gas from the 2-pentyl nitrite flask to obtain the pressure of interest, then slowly heating the water bath until boiling of the 2-pentyl nitrite sample was observed. Data points below room temperature were taken by using an ice water bath. Data points above room temperature were taken by heating the water bath. Vapor pressure data were taken over the temperature range 276 K – 343 K.

Figure A2 shows the natural logarithm of the vapor pressure of our sample plotted against the inverse boiling temperature. The plot is linear for temperatures up to 36 °C ($1000 / T > 3.23 \text{ K}^{-1}$). Above 36 °C, a brown gas evolved from the 2-pentyl nitrite sample, likely corresponding to decomposition of
the sample. We observe a kink in the vapor pressure plot, indicating that we may no longer be measuring the properties of 2-pentyl nitrite above 36 °C.

The data points prior to decomposition ($T < 36 \, ^\circ\text{C}$) can be fit to the Clausius-Clapeyron equation:

$$\ln p_{\text{vap}} = \left( -\frac{\Delta H_{\text{vap}}}{R} \right) \left( \frac{1}{T_{\text{vap}}} \right) + \left( \frac{\Delta H_{\text{vap}}}{RT_{\text{boil}}} + \ln p_{\text{atm}} \right) \tag{A1},$$

where $p_{\text{vap}}$ is the vapor pressure at temperature $T_{\text{vap}}$, $\Delta H_{\text{vap}}$ is the enthalpy of vaporization, $R$ is the universal gas constant, and $T_{\text{boil}}$ is the boiling point at atmospheric pressure $p_{\text{atm}}$. We assume a 4% uncertainty (2σ) on the vapor pressure data. Including both the error on each vapor pressure data point and overall scatter in the data points, we obtain $\Delta H_{\text{vap}} = 40.6 \pm 1.3 \text{ kJ mol}^{-1}$ and $T_{\text{boil, atm}} = (352 \pm 17) \text{ K}$. All uncertainties are reported to 2σ.

Although our data fit very well to Equation S1, it is important to emphasize that our 2-pentyl nitrite sample was not 100% pure. As described in the main text, the major contaminants were water [H$_2$O]:[RONO] = 1:14) pentanol (1:24), and NO (1:240). If an azeotrope of 2-pentyl nitrite forms with water or 2-pentanol, then the vapor pressure data may have additional error.
REFERENCES


Table 1 – Experimental conditions for spectra and relative kinetics

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<td><strong>Excimer Energy (248 nm)</strong></td>
<td>mJ / pulse</td>
<td>125</td>
</tr>
<tr>
<td><strong>Time after Photolysis</strong></td>
<td>µs</td>
<td>20</td>
</tr>
<tr>
<td><strong>N&lt;sub&gt;2&lt;/sub&gt; Purge Flow – Left Mirror</strong></td>
<td>sccm</td>
<td>500</td>
</tr>
<tr>
<td><strong>N&lt;sub&gt;2&lt;/sub&gt; Purge Flow – Right Mirror</strong></td>
<td>sccm</td>
<td>500</td>
</tr>
<tr>
<td><strong>N&lt;sub&gt;2&lt;/sub&gt; Bubbler Flow</strong></td>
<td>sccm</td>
<td>45</td>
</tr>
<tr>
<td><strong>O&lt;sub&gt;2&lt;/sub&gt; Dilution Flow</strong></td>
<td>sccm</td>
<td>3100 or 2700&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Residence Time</strong></td>
<td>ms</td>
<td>25</td>
</tr>
<tr>
<td><strong>Δτ/τ - Sensitivity (3660 cm&lt;sup&gt;-1&lt;/sup&gt;)</strong></td>
<td></td>
<td>0.4%</td>
</tr>
<tr>
<td>[RONO]</td>
<td>molec cm&lt;sup&gt;-3&lt;/sup&gt;</td>
<td>7 × 10&lt;sup&gt;15&lt;/sup&gt;e</td>
</tr>
<tr>
<td>Photolysis Flux (351 nm)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>photons cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>2 × 10&lt;sup&gt;17&lt;/sup&gt;</td>
</tr>
<tr>
<td>Photolysis Flux (248 nm)&lt;sup&gt;f&lt;/sup&gt;</td>
<td>photons cm&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>5 × 10&lt;sup&gt;16&lt;/sup&gt;</td>
</tr>
<tr>
<td><strong>Step Size</strong></td>
<td>cm&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.2</td>
</tr>
</tbody>
</table>

a) Temperature taken to be room temperature

b) Spectra were also recorded at 670 Torr, and observed to be equivalent to the spectra recorded under the conditions above

c) As described in the main text, relative kinetics data were taken by one of two methods: either by sitting at one frequency and scanning across a range of times after photolysis, or by measuring the entire ν<sub>1</sub> spectrum at a constant time after photolysis

d) The total of the N<sub>2</sub> and O<sub>2</sub> dilution flows was kept constant (3100 sccm for the spectroscopy experiments, 6000 sccm for the relative kinetics experiments). O<sub>2</sub> was set to 0 sccm to obtain HOR• spectra.

e) [RONO] calculated based on gas flows and p<sub>vap</sub>(273K)

f) The area of the excimer laser beam at the ringdown cell was 5 cm × 0.3 cm for all spectroscopy experiments at 351 nm, 3 cm × 1 cm for all spectroscopy experiments at 248 nm, and 6 cm × 0.2 cm for all kinetics experiments
Table 2 – Band positions and relative integrated absorbances for $\nu_1$ bands of HOR• and HOROO•

<table>
<thead>
<tr>
<th>$\nu_1$ (cm$^{-1}$)</th>
<th>HOR C$_4$H$_8$•</th>
<th>HOR C$_4$H$_8$OO•</th>
<th>HOR C$<em>4$H$</em>{10}$•</th>
<th>HOR C$<em>4$H$</em>{10}$OO•</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_{\text{HOR}} / I_{\text{HOROO}}$</td>
<td>1.0</td>
<td></td>
<td></td>
<td>1.2</td>
</tr>
<tr>
<td>$\nu_1$ (cm$^{-1}$) B3LYP/6-31+G(d,p)$^b$</td>
<td>3841</td>
<td>3842</td>
<td>3827</td>
<td>3829</td>
</tr>
<tr>
<td>$I / I_{\text{ROH}}$, B3LYP/6-31+G(d,p)</td>
<td>1.0</td>
<td>1.2</td>
<td>1.1</td>
<td>1.3</td>
</tr>
</tbody>
</table>

a) Calculated by using $k_{\text{isom}}/k_{O_2} = 1.7 \times 10^{19}$ cm$^{-3}$ for n-butoxy, $k_{\text{isom}}/k_{O_2} = 3.4 \times 10^{19}$ cm$^{-3}$ for 2-pentoxy

b) Unscaled harmonic frequencies
Table 3 – Rate constants, parameters, and correction factors used to calculate $k_{\text{isom}}/k_{\text{O}_2}$

<table>
<thead>
<tr>
<th>parameter</th>
<th>units</th>
<th>best value</th>
<th>uncertainty (2$\sigma$)</th>
<th>best value</th>
<th>uncertainty (2$\sigma$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_{\text{O}_2}$</td>
<td>$10^{19}$ cm$^{-3}$ s$^{-1}$</td>
<td>1.81</td>
<td>0.15</td>
<td>3.86</td>
<td>0.45</td>
</tr>
<tr>
<td>$k_{\text{isom}}$</td>
<td>$10^{14}$ cm$^{-3}$</td>
<td>1.40</td>
<td>0.70</td>
<td>0.80</td>
<td>0.40</td>
</tr>
<tr>
<td>$k_{\text{decomp}}$</td>
<td>$10^6$ s$^{-1}$</td>
<td>2.53</td>
<td>1.28</td>
<td>3.09</td>
<td>1.59</td>
</tr>
<tr>
<td>$k_{\text{NO}[NO]}$</td>
<td>s$^{-1}$</td>
<td>600</td>
<td>300</td>
<td>$2.0 \times 10^4$</td>
<td>$1.0 \times 10^4$</td>
</tr>
<tr>
<td>$\phi_{\text{pi}}$</td>
<td></td>
<td>0.038</td>
<td>0.018</td>
<td>0.049</td>
<td>0.024</td>
</tr>
<tr>
<td>$k_{\text{decomp}}/k_{\text{isom}}$</td>
<td></td>
<td>0.0024</td>
<td>0.0017</td>
<td>0.0648</td>
<td>0.0464</td>
</tr>
<tr>
<td>$k_{\text{NO}[NO]}/k_{\text{isom}}$</td>
<td></td>
<td>0.0262</td>
<td>0.0187</td>
<td>0.0215</td>
<td>0.0154</td>
</tr>
<tr>
<td>$X_{\text{kin}}$</td>
<td></td>
<td>0.97</td>
<td>0.02</td>
<td>0.92</td>
<td>0.04</td>
</tr>
<tr>
<td>$X_{\text{prompt}}$</td>
<td></td>
<td>0.96</td>
<td>0.02</td>
<td>0.95</td>
<td>0.02</td>
</tr>
<tr>
<td>$X_{\text{kin}} \times X_{\text{prompt}}$</td>
<td></td>
<td>0.93</td>
<td>0.03</td>
<td>0.87</td>
<td>0.04</td>
</tr>
<tr>
<td>$k_{\text{isom}}/k_{\text{O}_2}$</td>
<td>$10^{19}$ cm$^{-3}$</td>
<td>1.69</td>
<td>0.15</td>
<td>3.37</td>
<td>0.43</td>
</tr>
</tbody>
</table>

a) Ref 7
b) Estimated as
\[
\left( \frac{\partial \left( \frac{A_0}{A} \right)}{\partial [O_2]} \right)_{[O_2]=0} \times k_{\theta_2}
\]
c) Ref 72
d) Ref 65
Table 4 – Comparison of experimentally determined relative rate constant \( k_{\text{isom}}/k_{\text{O}2} \) and derived \( k_{\text{isom}} \) for \( n \)-butoxy and 2-pentoxy with previous measurements

<table>
<thead>
<tr>
<th>( n )-butoxy</th>
<th>( k_{\text{isom}}/k_{\text{O}2} ) ((10^{19} \text{ cm}^3))</th>
<th>( k_{\text{isom}} ) ((10^5 \text{ s}^{-1}))</th>
<th>molecules detected</th>
<th>method</th>
<th>( P ) (Torr)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )-butoxy</td>
<td>1.69 ± 0.15</td>
<td>2.37 ± 1.20</td>
<td>( \delta )-hydroxybutylperoxy</td>
<td>Slow flow, CRDS, ( \nu_1 )</td>
<td>670</td>
<td>This work</td>
</tr>
<tr>
<td>1.95 ± 0.4</td>
<td>2.73 ± 1.48</td>
<td>Butyl nitrite, Butanal, 4-hydroxy butanal</td>
<td>Static, FTIR</td>
<td>700</td>
<td>Cassanelli, 2006</td>
<td></td>
</tr>
<tr>
<td>1.5 ± 0.4</td>
<td>2.1 ± 1.2</td>
<td>Butane, Butanal</td>
<td>Static, GC</td>
<td>760</td>
<td>Cox, 1981</td>
<td></td>
</tr>
<tr>
<td>1.9 ± 0.4</td>
<td>2.7 ± 1.4</td>
<td>Butyl nitrite, Butanal</td>
<td>Static, FTIR</td>
<td>700</td>
<td>Niki, 1981</td>
<td></td>
</tr>
<tr>
<td>2.1 ± 0.5</td>
<td>2.9 ± 1.6</td>
<td>Butyl nitrite, Butanal</td>
<td>Slow flow, GC</td>
<td>760</td>
<td>Cassanelli, 2005</td>
<td></td>
</tr>
<tr>
<td>1.8 ± 1.1</td>
<td>2.5 ± 2.0</td>
<td>Butane, Butanal</td>
<td>Slow flow, GC</td>
<td>760</td>
<td>Cassanelli, 2005</td>
<td></td>
</tr>
<tr>
<td>1.8 ± 0.6</td>
<td>2.5 ± 1.5</td>
<td>Butanal, 4-hydroxy butanal</td>
<td>Static, FTIR</td>
<td>760</td>
<td>Geiger, 2002</td>
<td></td>
</tr>
<tr>
<td>0.25 ± 0.19f</td>
<td>0.35 ± 0.20f</td>
<td>OH and NO(_2)</td>
<td>Fast flow, A-X (OH), LIF (NO(_2))</td>
<td>38</td>
<td>Hein, 1999</td>
<td></td>
</tr>
<tr>
<td>1.6</td>
<td>2.2</td>
<td>Butanal</td>
<td>Static, GC</td>
<td>740</td>
<td>Carter, 1979</td>
<td></td>
</tr>
<tr>
<td>2.1 ± 1.8d</td>
<td>2.9 ± 1.4d</td>
<td>Butanal</td>
<td>Recommendation</td>
<td>760</td>
<td>IUPAC, 2006</td>
<td></td>
</tr>
</tbody>
</table>

| 2-pentoxy      | 3.37 ± 0.43                      | 2.70                        | \( \delta \)-hydroxy-\( n \)-pentyl peroxy | Slow flow, CRDS, \( \nu_1 \) | 670  | This work |
| 3.1e           | 2.5e                             | Pentane, 2-pentone | Static, GC | 700    | Atkinson, 1995 |
| 0.15           | 0.12f                           | Acetone, Acetaldehyde, 2-hexanol | Static, GC | 760    | Dóbé, 1986 |

a) All uncertainties are 2\( \sigma \). All studies other than the current work treat all alkoxy reactions besides isomerization and reaction with \( \text{O}_2 \) as negligible.
b) Computed \( k_{\text{isom}} \) assuming literature value of \( k_{\text{O}2} = (1.4 \pm 0.7) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \) for \( n \)-butoxy, \(^{26} \) and \( k_{\text{O}2} = 8 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \) for 2-pentoxy (no estimate available for the uncertainty). \(^7 \)
c) Unlike the other studies, Hein directly measured both \( k_{\text{isom}} \) and \( k_{\text{O}2} \). The \( k_{\text{isom}}/k_{\text{O}2} \) in the table is the ratio of their rate constants.
d) The IUPAC recommendation for \( k_{\text{isom}}/k_{\text{O}2} \) is computed from their individual recommendations of the isomerization and \( \text{O}_2 \) reactions.
e) The uncertainty on \( k_{\text{isom}}/k_{\text{O}2} \) is reported by Atkinson as a factor of 2.
f) Dóbé’s study calculates \( k_{\text{isom}} \) from the relative rate \( k_{\text{isom}}/k_{\text{decomp}} \) and their measured rate \( k_{\text{decomp}} = 1.2 \times 10^4 \text{ s}^{-1} \). The \( k_{\text{isom}}/k_{\text{O}2} \) reported in this table uses the literature value of \( k_{\text{O}2} = 8 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1} \) for 2-pentoxy. \(^7 \)
Table 5 – Partial derivatives of correction factors $X_{\text{kin}}$, $X_{\text{prompt}}$, and $X_{\text{kin}} \times X_{\text{prompt}}$ with respect to parameters $k_{\text{decomp}}/k_{\text{isom}}$, $k_{\text{NO}}[\text{NO}]/k_{\text{isom}}$, and $\phi_{\text{pi}}$

<table>
<thead>
<tr>
<th></th>
<th>n-butoxy</th>
<th>2-pentoxy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\partial X}{\partial (k_{\text{decomp}}/k_{\text{isom}})}$</td>
<td>-0.95</td>
<td>-0.04</td>
</tr>
<tr>
<td>$\frac{\partial X}{\partial (k_{\text{NO}}[\text{NO}]/k_{\text{isom}})}$</td>
<td>-0.95</td>
<td>-0.04</td>
</tr>
<tr>
<td>$\frac{\partial X}{\partial \phi_{\text{pi}}}$</td>
<td>0</td>
<td>-1.03</td>
</tr>
</tbody>
</table>
Table 6 – Percentage of HOC$_4$H$_8$OO$^\cdot$ in a hydrogen bound conformer based on our simple model and B3LYP/6-31+G(d,p) calculations

<table>
<thead>
<tr>
<th>$f \downarrow / D_0$ (cm$^{-1}$) $\rightarrow$</th>
<th>0</th>
<th>-160</th>
<th>-500</th>
<th>-1000</th>
<th>-1500</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>0.05</td>
<td>0%</td>
<td>1%</td>
<td>5%</td>
<td>38%</td>
<td>85%</td>
</tr>
<tr>
<td>0.10</td>
<td>1%</td>
<td>2%</td>
<td>11%</td>
<td>57%</td>
<td>92%</td>
</tr>
<tr>
<td>0.16</td>
<td>2%</td>
<td>4%</td>
<td>16%</td>
<td>69%</td>
<td>95%</td>
</tr>
<tr>
<td>0.20</td>
<td>2%</td>
<td>5%</td>
<td>21%</td>
<td>75%</td>
<td>96%</td>
</tr>
</tbody>
</table>
Figure Captions

**Figure 1** – Energy diagram for the decomposition, isomerization (left), and reaction with O\(_2\) (right), of \(n\)-butoxy radicals. Energies for the decomposition and isomerization are taken from Somnitz and Zellner\(^5,23\) at the modified G2(MP2,SVP) level of theory, while energies for the reaction with O\(_2\) are taken from Jungkamp et al.\(^6\) at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G(d,p) level of theory. All energies listed are relative to the \(n\)-butoxy radical.

**Figure 2** – Diagram of the PLP-CRDS gas kinetics cell. The spectra reported in this work were recorded at 300 Torr and 295 K. Typical residence time for the gases was 25 ms. The relative kinetics data were recorded at 670 Torr and 295 K. Typical residence time for the gases was 75 ms.

**Figure 3** – Diagram of the PLP-CRD spectrometer used to measure spectra in the mid-IR (2.7 – 3.7 \(\mu\)m). Alkoxy radicals were generated by photolysis of alkyl nitrites by an excimer laser. Mid-IR light was generated by sending the outputs of a Nd:YAG laser and a Nd:YAG pumped dye laser to an optical parametric amplifier, then filtering the visible light.

**Figure 4** – Cavity loss (mirror reflectivity plus absorption) of the precursor chemicals (excimer off) and the photolysis products (excimer on) in the mid-IR for \(n\)-butyl nitrite (a, 300 Torr) and 2-pentyl nitrite (b, 315 Torr). All spectra were taken at room temperature (295 ± 2 K) and \([\text{O}_2]\) = 1 \(\times\) 10\(^{18}\) molec cm\(^{-3}\), 0.2 cm\(^{-1}\) between data points. The alkyl nitrite absorptions show considerable structure across the entire region. The large peak in the 2-pentyl nitrite spectrum centered at 3660 cm\(^{-1}\) is due to residual 2-pentanol. Additional absorption features are observed following photolysis of the alkyl nitrite.
Figure 5 – \( \nu_1 \) (OH stretch) spectra of the isomerization of products of \( n \)-butoxy, in the absence (\( \delta \)-HOC\(_4\)H\(_8\)•, a) and presence of O\(_2\) (\( \delta \)-HOC\(_4\)H\(_8\)OO•, b, [O\(_2\)] = 9 \times 10^{17} \) molec cm\(^{-3}\)). Spectra were recorded at 295 K, 300 Torr, 0.2 cm\(^{-1}\) between data points, 20 \( \mu \)s after photolysis of \( n \)-butyl nitrite, [RONO] = 7 \times 10^{15} molec cm\(^{-3}\), with a 1.5% photolysis ratio. The \( \delta \)-HOC\(_4\)H\(_8\)• spectrum was signal averaged for 4.8 s per points, while the \( \delta \)-HOC\(_4\)H\(_8\)OO• spectrum was signal averaged for 8.0 s per point. Both spectra are similar in position and shape to the FTIR spectrum of \( n \)-butanol (a, shown in green). Assuming an isomerization rate constant \( k_{\text{isom}} = 2.4 \times 10^5 \) s\(^{-1}\), we predict that in the absence of O\(_2\), 94% of the product being measured is HOC\(_4\)H\(_8\)•, and 6% is its dimer, HOC\(_8\)H\(_{16}\)OH. In the presence of O\(_2\), we predict that 98% of the product being measured is HOC\(_4\)H\(_8\)OO• and 2% are other secondary products.

Figure 6 – \( \nu_1 \) (OH stretch) spectra of the isomerization of products of 2-pentoxy, in the absence (\( \delta \)-HO-1-C\(_5\)H\(_{10}\)•, a) and presence of O\(_2\) (\( \delta \)-HO-1-C\(_5\)H\(_{10}\)OO•, b, [O\(_2\)] = 1 \times 10^{18} \) molec cm\(^{-3}\)). Spectra were recorded at 295 K, 315 Torr, 0.2 cm\(^{-1}\) between data points, 20 \( \mu \)s after photolysis of 2-pentyl nitrite, [RONO] = 7 \times 10^{15} molec cm\(^{-3}\). The photolysis ratio is not well known: if the UV cross section of 2-pentyl nitrite is taken to be equal to \( n \)-butyl nitrite, then \( [RO•]_0 = 1 \times 10^{14} \) molec cm\(^{-3}\). The peak intensities suggest that \( [HOR•]_0 = 5 \times 10^{13} \) molec cm\(^{-3}\). Both the \( \delta \)-HO-1-C\(_5\)H\(_{10}\)• and \( \delta \)-HO-1-C\(_5\)H\(_{10}\)OO• spectra were signal averaged for 11.2 s per point. Both spectra are similar in position and shape to the FTIR spectrum of 2-pentanol (a, shown in green). Assuming an isomerization rate constant \( k_{\text{isom}} = 2.4 \times 10^5 \) s\(^{-1}\), we predict that in the absence of O\(_2\), 94% of the product being measured is \( \delta \)-HO-1-C\(_5\)H\(_{10}\)•, and 6% is its dimer, HOC\(_{10}\)H\(_{20}\)OH. In the presence of O\(_2\), we predict that 98% of the product being measured is \( \delta \)-HO-1-C\(_5\)H\(_{10}\)OO• and 2% are other secondary products.

Figure 7 – Infrared spectra of the products formed from photolysis of isobutyl nitrite and tert-butyl nitrite. Spectra were recorded at 295 K, 300 Torr, 0.2 cm\(^{-1}\) between data points, 20 \( \mu \)s after photolysis of
the alkyl nitrite, \([\text{RONO}] = 8.1 \times 10^{15} \text{ molec cm}^{-3}\), with a 1.2\% photolysis ratio. No absorption features in the \(\nu_1\) region are observed, indicating that the products of isobutoxy and tert-butoxy chemistry do not contain hydroxyl groups.

**Figure 8** – Absorbance at \(3662 \text{ cm}^{-1}\) for \(n\)-butoxy isomerization as a function of time after \(n\)-butyl nitrite photolysis. Data were recorded at 295 K, 300 Torr, \([\text{O}_2] = 9 \times 10^{17} \text{ molec cm}^{-3}\), \([\text{RONO}] = 7 \times 10^{15} \text{ molec cm}^{-3}\), with a 1.6\% photolysis ratio. The absorbance reaches its maximum within 20 \(\mu\)s of photolysis and remains constant thereafter.

**Figure 9** – Figure 9a – Infrared spectra of the photolysis products of \(n\)-butyl nitrite at \(248 \text{ nm}\) (red dotted line) and \(351 \text{ nm}\) (black solid line). Spectra were taken at 295 K, 670 Torr, \([\text{O}_2] = 0 \text{ Torr}\). The \(351 \text{ nm}\) spectrum has been scaled up by a factor of 3.1 so that the areas of the HOR are equal. Figure 9b – Infrared spectra of the photolysis products of \(2\)-pentyl nitrite at \(351 \text{ nm}\), 295 K, 670 Torr, \([\text{O}_2] = 0 \text{ Torr}\). The absorption at \(3470 \text{ cm}^{-1}\) is assigned to formaldehyde (Figure 9a) or acetaldehyde (Figure 9b), formed through prompt decomposition of the alkoxy radicals when generated through photolysis. On the basis of the observed absorptions and relative cross sections, \(^{77}\) we estimate a prompt decomposition ratio \(\phi_{pd} = 0.77 \pm 0.14 (2\sigma)\) for \(n\)-butoxy following \(248 \text{ nm}\) photolysis. We place upper limits of \(\phi_{pd} = 0.11\) for \(n\)-butoxy following \(351 \text{ nm}\) photolysis and \(\phi_{pd} = 0.26\) for \(2\)-pentoxy following \(351 \text{ nm}\) photolysis, based on the noise level of our spectrometer in the \(2\nu_2\) region.

**Figure 10** – \(A_0/A\) plotted as a function of \([\text{O}_2]\) for \(n\)-butoxy (part a) and \(2\)-pentoxy (part b) using the \(\nu_1\) CRDS absorbance. Both plots show the expected decrease in \(A/A_0\) with \([\text{O}_2]\). For \(0 < [\text{O}_2] < 3 \times 10^{16} \text{ molec cm}^{-3}\), the \(n\)-butoxy data show an apparent increase in \(A/A_0\) with \([\text{O}_2]\) (points marked by red Xs in part a, expanded in Figure 11). Only the data with \([\text{O}_2] > 1 \times 10^{17} \text{ molec cm}^{-3}\) were used in the fits to determine...
$k_{\text{isom}} / k_{O_2}$. Figure 10(a): slope = $(5.56 \pm 0.43) \times 10^{-20}$ cm$^3$, intercept = $1.01 \pm 0.04$, $k_{\text{isom}} / k_{O_2} = (1.69 \pm 0.15) \times 10^{19}$ cm$^3$. Figure 10(b): slope = $(2.59 \pm 0.29) \times 10^{-20}$ cm$^3$, intercept = $1.00 \pm 0.03$, $k_{\text{isom}} / k_{O_2} = (3.37 \pm 0.43) \times 10^{19}$ cm$^3$. The reported $k_{\text{isom}} / k_{O_2}$ include the correction factors of $0.93 \pm 0.03$ and $0.87 \pm 0.04$ to account for additional reaction pathways, as described in the text. All uncertainties are reported to $2\sigma$. As described in the text, our data indicate that 4% of the $n$-butoxy radicals and 5% of the 2-pentoxy radicals undergo prompt isomerization. A fit to the data assuming 0% (green) or 20% (red) prompt isomerization is shown for reference. Our data are not fit well if large amounts of prompt isomerization are assumed.

**Figure 11** – $A_0/A$ plotted as a function of [O$_2$] for $n$-butoxy for $0 < [O_2] < 3 \times 10^{16}$ molec cm$^{-3}$. In this region, the $n$-butoxy data show an apparent increase in $A/A_0$ with [O$_2$], consistent with the change in product being detected (HOR$\bullet$ at [O$_2$] = 0 Torr, HOROO$\bullet$ for [O$_2$] > $3 \times 10^{16}$ molec cm$^{-3}$), as described in the text. Because of this effect, only absorbance data with [O$_2$] > $1 \times 10^{17}$ molec cm$^{-3}$ were used in the fits to determine $k_{\text{isom}} / k_{O_2}$.

**Figure A1** – Apparatus used to measure the vapor pressure of 2-pentyl nitrite

**Figure A2** – Clausius-Clapeyron plot for the 2-pentyl nitrite used for the spectra reported in this work. The data are non-linear above 36°C ($1000 / T < 3.24$ K$^{-1}$) due to decomposition of the 2-pentyl nitrite. We report the $2\sigma$ uncertainty on each vapor pressure as ± 4%. The best fit line to data points at or below 36°C gives slope = $(-4900 \pm 150)$ K, intercept = $20.5 \pm 0.5$. Using these values, $\Delta H_{\text{vap}} = 40.6 \pm 1.3$ kJ mol$^{-1}$ and $T_{\text{boil},1\text{ atm}} = (352 \pm 17)$ K. All uncertainties are reported to $2\sigma$. 
FIGURES

Figure 1

![Graph showing energy levels and reaction paths.](image)

Figure 2

![Diagram illustrating a reaction setup.](image)
Figure 3

![Diagram showing various laser and detector systems](image)

Figure 4

![Graphs showing frequency and cavity loss for different compounds with and without excimer](image)

\[ \text{a) } \text{C}_4\text{H}_9\text{ONO} + \text{hv} \]

\[ \text{b) } \text{C}_5\text{H}_{11}\text{ONO} + \text{hv} \]
Figure 5

![Graph showing frequency (cm⁻¹) against absorbance (ppm) for n-butanol (green) and δ-HOC₄H₈OO⁻ (black).](image)

Figure 6

![Graph showing frequency (cm⁻¹) against absorbance (ppm) for δ-HOC₄H₈OO⁻.](image)
a) \(2\text{-C}_2\text{H}_5\text{OH (FTIR)}\)

\(\delta\text{-HOC}_5\text{H}_{10}\)

b) \(\delta\text{-HOC}_5\text{H}_{10}\text{OO}^-\)
Figure 7

![Graph showing frequency vs. absorbance for isobutoxy and tert-butoxy]

Figure 8

![Graph showing time after photolysis vs. absorbance for n-butoxy: δ-HOC₄H₆OO⁻]

Absorbance (ppm)

Time after photolysis (µs)
Figure 9(a,b)

(a) n-butoxy

248 nm

351 nm (scaled up by 3.1)

Absorbance (ppm)

Frequency (cm$^{-1}$)

Figure 10(a,b)

(b) 2-pentoxy, 351 nm

Absorbance (ppm)

Frequency (cm$^{-1}$)
Figure 11

[Graph showing the relationship between \([O_2]\) and \(A_0/A\) for \(n\)-butoxy, low \([O_2]\)]

Figure A1

[Diagram depicting a schematic of a vacuum setup involving air inlet, vacuum pump, thermometer, baratron, and a water bath labeled 2-pentyl nitrite, with temperature range 0 – 70 °C]
Figure A2

2-C_{5}H_{11}ONO

Best fit line through $T \leq 36^\circ C$