Isomerization of Alkoxy Radicals under Atmospheric Conditions

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The reactions of the 2-hexoxy radical and the 3-hexoxy radical have been studied in a collapsible Teflon bag reactor under conditions relevant to the atmosphere. The alkoxy radicals were generated either by the photolysis of the corresponding hexyl nitrite or by the OH radical initiated photooxidation of hexane. The alkoxy radicals were chosen as model species to examine the importance of alkoxy radical isomerization versus unimolecular decomposition or reaction with oxygen. The fraction of 2-hexoxy radicals undergoing isomerization was determined directly from the analysis of the 5-hydroxyhexan-2-one product. The fraction of 3-hexoxy radicals undergoing isomerization could only be determined indirectly. The formation of products proposed to be generated from the isomerization reaction channels was observed for the first time, including 5-nitrooxyhexan-2-ol from the reaction of isomerized radicals with NO. The approximate quantitative results confirm the predicted dominance of isomerization (>68%) over other reaction pathways for longer chain alkoxy radicals. The results are compared with predictions based on kinetic estimations.

Introduction

The potential of an organic compound to generate ozone in the troposphere is determined not only by the rate with which it reacts with OH radicals but also by the nature of the products formed. The hydroxyl radical-initiated photooxidation of an organic compound in air containing NO is believed to lead to the generation of alkoxy radicals as shown in the following general reaction scheme (1).

\[
RCH_2R' + OH \rightarrow RCHR' + H_2O \quad (1)
\]

\[
RCHR' + O_2 + M \rightarrow RCH(0)OR' + M \quad (2)
\]

\[
RCH(0)OR' + NO \rightarrow RCH(0)OR' + NO_2 \quad (3a)
\]

\[
RCH(0)OR' + NO + M \rightarrow RCH(ONO)_2OR' + M \quad (3b)
\]

The reactions of the alkoxy radicals formed in reaction 3 are largely responsible for the observed product distributions from the photooxidation of organic compounds under conditions typically found in the polluted troposphere. Alkoxy radicals may react further by reaction with oxygen (reaction 4a), by unimolecular decomposition (reaction 4b), and in the case of \( \geq C_4 \) alkoxy radicals by isomerization (reaction 4c) (2).

\[
RCH(0)OR' + O_2 \rightarrow RC(0)OR' + HO_2 \quad (4a)
\]

\[
RCH(0)OR' \rightarrow R' + RCHO \quad (4b)
\]

\[
RCH(0)OR' \rightarrow RCH(0H)OR'' \quad (4c)
\]

Isomerization has been suggested to occur via a six-membered or a five-membered ring intermediate. The formation of the five-membered ring intermediate involves more strain, and this isomerization process is therefore assumed to be slower than the isomerization reaction via the six-membered ring intermediate (2).

To the best of our knowledge, there is no direct experimental evidence for the occurrence of the isomerization processes (reaction 4c) by way of specific product identification under atmospheric conditions. Indirect evidence for alkoxy radical isomerization was found in photooxidations of \( C_4-C_6 \) \( n \)-alkanes (3) in which the formation of carbonyl products (reactions 4a and 4b) fell considerably short of the consumption of \( n \)-alkane. In studies with butane, Carter et al. (4) and Cox et al. (5) derived a rate constant ratio, \( k_{4c}/k_{4a} \), for the \( n \)-butoxy radical based on the yields of \( n \)-C\(_2\)H\(_4\)CHO (reaction 4a) and the rate of conversion of \( n \)-C\(_4\)H\(_{10}\). Niki et al. (6) reported a similar value of \( k_{4c}/k_{4a} \) for the \( n \)-butoxy radical from an FT/IR study of the photolysis of \( n \)-butyl nitrite in the presence of \( O_2 \), measured on the basis of the rate of conversion of \( n \)-butyl nitrite. The rate constant ratios derived in these three studies are in good agreement, with an average value of \( k_{4c}/k_{4a} = 1.7 \times 10^{19} \) molecule cm\(^{-2}\) at 299 K. Niki et al. (6) found in the same FT/IR study products with O-H and C-OH stretching modes, which can be taken as indicating the occurrence of the isomerization of the \( n \)-butoxy radical, but they could not assign these vibrations to any specific compounds. Döbé et al. (7) produced 2-pentoxy radicals.

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from the photolysis of di-2-pentyl peroxide in the presence of a relatively high concentration of CH$_3$ radicals and observed the product CH$_3$CHOH(CH$_2$)$_3$CH$_3$ from the combination of the isomerized 2-pentoxy radical (reaction 4c) with CH$_3$.

In the present study the reactions of 2- and 3-hexoxy radicals were investigated by end-product analysis in a collapsible Teflon bag reactor under conditions relevant to the polluted troposphere. Hexoxy radicals were chosen as surrogates to investigate the importance of isomerization pathways for alkoxyl radicals. The hexoxy radicals were produced either by the photolysis of the corresponding hexyl nitrite or by the OH-initiated photooxidation of hexane generating mainly 2- and 3-hexoxy radicals from secondary C–H abstraction rather than from primary C–H. Hexane is present in the troposphere through its use as a solvent and as a component of gasoline.

Bag reactor experiments can be influenced by adsorption processes on the reactor walls. The material adsorbed on the Teflon film was analyzed in order to assess the influence from the bag at a flow rate of 80 cm$^3$ min$^{-1}$ through two tubes. A sample of 320 cm$^3$ of the gas mixture was drawn onto the chromatographic column. The trap was heated up to 473 K by means of a cold trap (Carlo Erba) before injection for up to 50 min. The decay of the alkyl nitrite concentration and buildup of the product concentrations were monitored during the course of the experiment.

The concentration of the alkyl nitrite was measured by GC/ECD (Carlo Erba) by withdrawing 3 cm$^3$ samples from the bag via a gas-sampling valve. The alkyl nitrite was separated from the products, which were not identified in this analysis, using a 15 m, 0.32 mm i.d., 4.8 $\mu$m film PS-255 column (11) at 343 K. The detector response was calibrated by preparing authentic samples of the alkyl nitrite in nitrogen.

Samples for qualitative GC/MS analysis from selected experiments were preconcentrated on Tenax TA adsorption tubes. A sample of 320 cm$^3$ of the gas mixture was drawn from the bag at a flow rate of 80 cm$^3$ min$^{-1}$ through two tubes in series (9). The contents of the tubes were thermally desorbed (Carlo Erba TDAS 5000) at 473 K for 10 min into a stream of helium. The sample was reconcentrated at 123 K by means of a cold trap (Carlo Erba) before injection onto the chromatographic column. The trap was heated rapidly to 473 K to inject the sample onto a 30 m, 0.25 mm i.d., 1 $\mu$m film DB-1701 capillary column (J & W Scientific). The column was kept at 308 K for 10 min and then heated up to 473 K at a heating rate of 5 K min$^{-1}$. Detection was performed with EI/MS (Finnigan 4500). To investigate the possibility of thermal decomposition of adsorbed species during the analytical procedure, the contents of some of the adsorption tubes were desorbed at 423 K, and the cold trap was heated to only 423 K.

The carbonyl products were quantitatively determined by derivatization with 2,4-dinitrophenylhydrazine (2,4-DNPH) followed by HPLC separation using a three-component gradient solvent program and UV detection (12). Samples of 4 dm$^3$ were withdrawn from the bag reactor at a flow rate of 1 dm$^3$ min$^{-1}$ through two impingers in series containing 4 cm$^3$ of acidified 2,4-DNPH solution (9). The samples were left to stand overnight to allow hexan-2,5-dione to be completely derivatized. To calibrate the detector response, the hydrazone derivatives were prepared, and liquid samples were injected into the HPLC. The sampling efficiencies were derived by preparing known mixtures of the carbonyl compounds in nitrogen in the bag reactor and comparing the response to the liquid standards (9).

OH-Initiated Photooxidation of Hexane. Hydroxyl radicals were generated from the photolysis (350–450 nm) of nitrous acid vapor in synthetic air. Nitrous acid vapor was produced by the reaction of aqueous sodium nitrite with sulfuric acid (13). The mixtures contained typically 4 ppmv HONO with ca. 1.6 and 0.9 ppmv each of NO and NO$_2$ produced as byproducts of the nitrous acid generation. Hexane (9–15 ppmv) was added to the mixture by sweeping the contents of a calibrated volume into the bag reactor with a stream of synthetic air. The same procedure was followed to equilibrate and irradiate the gas mixture as described above. In these experiments, the bag mixture was irradiated for up to 1 h, and the decay of the hexane concentration and buildup of the product concentrations were monitored during the course of the experiment. The concentrations of nitrogen oxides (NO + NO$_2$ + HONO) were monitored by chemiluminescent analysis (Thermo Environmental Inc. Model 42).

The concentration of hexane was measured by GC/FID (Carlo Erba) by withdrawing 6 cm$^3$ samples from the bag via a gas-sampling valve. Hexane was separated from the products, which were not identified in this analysis, using a 20 m, 0.32 mm i.d., 4.8 $\mu$m film OV-1701 column (11) at 308 K. The detector response was calibrated by preparing standard mixtures of hexane in nitrogen.

The formation of alkyl nitrates and hexanones was measured by GC with sample preconcentration using the Tenax TA adsorption tubes. The sampling conditions were as described above for the GC/MS analysis. The contents of the tubes were desorbed at 423 K for 10 min into a stream of hydrogen. The sample was reconcentrated at 123 K by means of the cold trap. The trap was heated rapidly to 423 K to inject the sample onto the DB-1701 capillary column employed in the product analysis from the alkyl nitrite experiments. The column was kept at 308 K for 10 min and then heated up to 473 K at a heating rate of 10 K min$^{-1}$. Detection was performed with FID and ECD coupled in series. The detector responses were calibrated by preparing mixtures containing known concentrations of the compounds in nitrogen. Sample breakthrough in the collection procedure was checked by the use of two adsorption tubes.
in series. The amount of material found on the backup tube was always <1% of that on the primary tube.

The GC/MS analysis for selected experiments and the analysis of carbonyl products were conducted as described above. Fractions of some of the unknown hydrazine derivatives were collected after the HPLC separation, concentrated, and then injected into a mass spectrometer (VG AutoSpec-Q) using a solid probe inlet.

**Analysis of Material Trapped on Walls of Bag Reactor.** Special Teflon bags were constructed to study the adsorption of products on the reactor walls. Pieces of Teflon film were sealed inside the Teflon bags at a seam. Following a 234 thermal desorption at 423 K and analyzed by GC/FID/EC and GC/MS following the same procedures as described above.

**Materials.** 2-Hexyl nitrite and 3-hexyl nitrite were prepared by the reaction of the corresponding alcohol with nitrous acid (14). The purity of the product was checked by FT/IR, NMR, and GC/ECD. 2- and 3-hexyl nitrates and n-butyl nitrate were prepared by the reaction of the corresponding alcohol with nitric acid (15). The purities of the products were checked by FT/IR and GC/ECD. 5-Hydroxyhexan-2-one was prepared by the reaction of hexan-2,5-diol with the chromium trioxide-pyridine complex (16) and was separated from hexan-2,5-dione by column chromatography. The structure and purity of the product was checked by NMR. Hexan-2,5-diol was prepared by the hydrogenation of hexan-2,5-dione with lithium aluminium hydride in diethyl ether. 5-Nitrooxyhexan-2-ol was prepared by protecting one of the OH groups in butylalcohol in pentane with diisobutylaluminium hydride (17) and was separated from hexan-2,5-dione by column chromatography. The unprotected hydroxy group was reacted with nitromethane. This procedure lead directly to sufficient yields of the unprotected product. The structure of the product was checked by NMR. An attempt was made to prepare 4-hydroxybutan-1-ol by the reaction of γ-butyrolactone in pentane with diisobutylaluminium hydride in hexane (18), but NMR analysis showed that the reaction product was mostly in the form of the cyclic isomer, tetrahydro-1-hydroxy furan. The following chemicals were used without further purification other than bulb-to-bulb distillation: hexane (Fluka, >99.7%), methanal (Fluka), ethanal (Fluka, >99.5%), propanal (Merck, >98%), butanal (Fluka, >99%), hexan-2-one (Merck, >98%), hexan-3-one (Merck, >96%), and hexan-2,5-dione (Merck, >97%).

**Results**

2-Hexyl Nitrite Photolysis in Synthetic Air—NO Mixtures. The initial conditions for the experiments conducted are shown in Table 1. The products which were identified and quantified by HPLC as the 2,4-DNPH derivatives include methanal, ethanal, propanal, butanal, and hexan-3-one. Two significant peaks could not be identified. In the GC/MS analysis, hexan-3-one, hexan-3-ol, and 2-ethylfuran were identified by comparison to library spectra. Four major peaks and a number of minor peaks could not be identified. Hexan-2-one and hexan-2-ol were present prior to the irradiation and are thought to arise from the thermal decomposition of the alkyl nitrite in the analytical procedure because these compounds were not observed when checking the purity of the nitrite.

3-Hexyl Nitrite Photolysis in Synthetic Air—NO Mixtures. The initial conditions for the experiments conducted are shown in Table 1. The products which were identified and quantified by HPLC as the 2,4-DNPH derivatives include methanal, ethanal, propanal, butanal, and hexan-3-one. Two significant peaks could not be identified. In the GC/MS analysis, hexan-3-one, hexan-3-ol, and 2-ethylfuran were identified by comparison to library spectra. Four major peaks and a number of minor peaks could not be identified. Hexan-3-one and hexan-3-ol were present prior to the irradiation and are thought to arise from the thermal decomposition of the alkyl nitrite in the analytical procedure as discussed for the photolysis of 2-hexyl nitrite.

**OH Radical-Initiated Photooxidation of Hexane.** The initial conditions for the experiments conducted are shown in Table 1. The products which were identified and quantified by HPLC as the 2,4-DNPH derivatives include methanal, ethanal, propanal, butanal, and 5-hydroxyhexan-2-one. Hexan-2,5-dione was quantified but is thought to be a secondary product. One peak could not be identified, but the retention time corresponds to one of the unknown compounds observed in the 3-hexyl nitrite photoysis. Hexan-2-one and hexan-3-one could not be separated using this method and were quantified using the measurements from the thermal desorption method (see below).

The primary products which were quantified using the thermal desorption method include 2-hexyl nitrate, 3-hexyl nitrate, n-butyl nitrate, hexan-2-one, and hexan-3-one. These compounds were identified for quantification by retention time. The retention times were confirmed in the GC/MS analysis. 5-Nitrooxyhexan-2-ol was detected, but reliable quantification was not possible.

In the GC/MS analyses, hexane, cyclohexane, butanal, n-butyl nitrate, 2-ethylfuran, 2,5-dimethylfuran, tetrahydro-2,5-dimethylfuran, hexan-2-one, hexan-2-ol, hexan-3-one,
hem-3-01, hexan-2,5-dione, and benzaldehyde were identified by comparison with library spectra. 2-Hexyl nitrate and 3-hexyl nitrate were identified by comparison with spectra acquired from the prepared standards. Cyclohexane was found and is an impurity present in hexane. Benzaldehyde can be formed when Tenax is exposed to ozone (20, 21). Eight major peaks and a number of minor peaks could not be identified. Two of these major peaks corresponded to unidentified major peaks in the 2-hexyl nitrite experiments; four major peaks corresponded to the unidentified major peaks in the 3-hexyl nitrite experiments.

**Confirmation of Identification of 5-Hydroxyhexan-2-one.** 5-Hydroxyhexan-2-one could not be identified by GC/MS but was identified by the retention time of its 2,4-DNPH derivative in the HPLC analysis. Fractions of the derivative collected from HPLC and the derivative from the prepared standard of 5-hydroxyhexan-2-one were analyzed by MS using a solid probe inlet. This analysis lead to the correct determination of the molecular mass. The peak attributed to 5-hydroxyhexan-2-one was not observed in the 3-hexyl nitrite photolysis experiments. This confirms that this compound can be separated from its isomer arising from the 3-hexoxy radical isomerization. We performed calibrations using both the prepared standard of 5-hydroxyhexan-2-one and the collected fraction, which were in agreement within reasonable error limits. This result makes the coelution with other isomers seem rather unlikely.

Previous studies of the HPLC analyses of the 2,4-DNPH derivatives of hydroxyethanol and hydroxyacetone by Grosjean et al. (22) have reported the formation of double derivatives of these compounds, arising from the conversion of the hydroxy carbonyls to bicarbonyls in the derivatization process. In the present study, we found no evidence for the formation of a double 2,4-DNPH derivative in the analyses of 5-hydroxyhexan-2-one with our standard sample of this compound.

**Material Adsorbed on Walls of the Bag Reactor.** The Teflon stripes placed in the adsorption tubes were weighed, and the surface area was calculated knowing the thickness and the density of the Teflon film. The total amount of a species adsorbed was then estimated, assuming uniform adsorption on the surface of the bag. The total amount of adsorbed material was normalized to the initial concentration of hexane present. The compounds identified using GC/MS by comparison with library mass spectra include 2-ethylfuran, 2,3-dihydrofuran, and tetrahydro-2,5-dimethylfuran. 2-Hexyl nitrate, 3-hexyl nitrate, and 5-nitrooxyhexan-2-ol were identified by comparison to mass spectra acquired from the prepared standards. Ten peaks could not be identified. The compounds identified and quantified using GC/FID/ECD include 3-hexyl nitrate, 2-hexyl nitrate, and 5-nitrooxyhexan-2-ol. The ratio of the amount of the hexyl nitrate found on the wall of the bag to the amount detected in the gas phase using the adsorption tubes was found to be \( \approx 0.01 \). The same ratio for 5-nitrooxyhexan-2-ol was found to be about 0.4.

**Discussion**

The observed product distributions will be discussed in terms of the general reaction scheme, reactions 1–4 presented earlier, as applied to the specific radicals of the present study.

**2-Hexoxy Radical Reactions from Photolysis of 2-Hexyl Nitrite.** The photolysis of 2-hexyl nitrite is assumed to occur mainly via the homolytic cleavage of the RO–NO bond (23) to yield a 2-hexoxy radical and NO.

\[
\text{CH}_3\text{CH}[(\text{ONO})(\text{CH}_2)_3\text{CH} + \text{hv} \rightarrow \text{CH}_3\text{CH}[(\text{O})\text{(CH}_2)_3\text{CH} + \text{NO} \quad (5)
\]

According to the general reaction scheme proposed, the 2-hexoxy radical may react with oxygen (reaction 6a), decompose (reactions 6b and 6c), isomerize by 1,5-H shift (reaction 6d), or isomerize by 1,4-H shift (reaction 6e) (see Figure 1).

The methyl radical formed in reaction 6b will react with \( \text{O}_2 \) and NO to form methanol (1). The \( n \)-butyl radical formed in reaction 6c may react further with \( \text{O}_2 \) and NO (reactions 7, 8a, and 8b). The \( n \)-butoxy radical formed in reaction 8a may react further by reaction with \( \text{O}_2 \) (reaction 9a), by decomposition (reaction 9b), or by 1,5-H shift isomerization (reaction 9c). The \( n \)-propyl radical formed in reaction 9b is thought to react with \( \text{O}_2 \) and NO to form propenal (reaction channel 10) (1). The radical formed in reaction 9c will react with \( \text{O}_2 \) and NO to form the 4-hydroxy-1-butoxy radical. This radical is thought to isomerize.

\[
\text{OCH}_2(\text{CH}_2)_2\text{CHOH} + \text{O}_2 \rightarrow \text{HOCH}_2(\text{CH}_2)_2\text{CHOH} \quad (11)
\]

In this case, isomerization is estimated to be very rapid as a secondary hydrogen atom is being abstracted from a carbon atom with an OH group substituent (1). The \( \alpha \)-hydroxalkyl radical formed in reaction 11 will then react with oxygen to form 4-hydroxybutan-1-ol plus an \( \text{HO}_2 \) radical rather than to form a peroxy radical (2).

\[
\text{HOCH}_2(\text{CH}_2)_2\text{CHOH} + \text{O}_2 \rightarrow \text{HOCH}_2(\text{CH}_2)_2\text{CHOH} + \text{HO}_2 \quad (12)
\]

The 5-hydroxy-2-hexyl radical formed by 1,5-H shift isomerization in reaction 6d is thought to react further with \( \text{O}_2 \) (reaction 13) and NO (reactions 14a and 14b). The radical formed in reaction 14a may react further by 1,5-H shift isomerization (reaction 15). In this case, isomerization is estimated to be even more likely than in the case of reaction 6d as a secondary hydrogen atom is being abstracted from a carbon atom with an OH group substituent (1). The \( \alpha \)-hydroxalkyl radical formed in reaction 11 will react with \( \text{O}_2 \) (reaction 16) as proposed above for the radical formed in reaction 11. 5-Hydroxyhexan-2-one formed in reaction 16 could undergo secondary photooxidation through attack by \( \text{OH} \) radicals with 72% of the \( \text{OH} \) radical reaction estimated to occur at the tertiary carbon atom (24) (reaction 17), which could lead to the formation of hexan-2,5-dione (reaction 18).

\[
\text{CH}_3\text{C}(\text{O})\text{(CH}_2)_2\text{CH(OH)}\text{CH}_3 + \text{OH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{(CH}_2)_2\text{C(OH)}\text{CH}_3 + \text{H}_2\text{O} \quad (17)
\]

\[
\text{CH}_3\text{C}(\text{O})\text{(CH}_2)_2\text{C(OH)}\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{(CH}_2)_2\text{C(O)}\text{CH}_3 + \text{HO}_2 \quad (18)
\]

The observed products, with the proposed reaction sources, were as follows: hexan-2-one consistent with reaction 6a, methanal from the methyl radical (formed in reaction 6b) and formed in reaction 9b, ethanal formed in reaction 6c, \( n \)-butyl nitrate formed in reaction 8b, butanal formed in reaction 9a, propenal formed from the \( n \)-propyl

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FIGURE 1. Schematic representation of the reactions of the 2-hexoxy radical under tropospheric conditions. The observed products are drawn in boxes.

radical formed in reaction 9b, 5-hydroxyhexan-2-one formed in reaction 16, and hexan-2,5-dione formed in reaction 18. Pentanal, proposed to be formed in reaction 6b, was not observed. The formation of 4-hydroxybutanal-1-al (reaction 12) could not be confirmed. The attempted synthesis of that compound lead mostly to the cyclic isomer tetrahydro-1-hydroxyfuran, which was not observed as a reaction product.

The fractions of 2-hexoxy radicals proceeding through reactions 6a–6e can be found by plotting the yields of the products versus the decrease in 2-hexyl nitrite due to photolysis. Typical plots are shown for run 3 in Figure 2. The results from such plots for all experiments are shown in Table 2. The fractions were calculated without applying any correction for secondary photooxidation since the OH radical concentration for the experimental conditions is not known. OH radicals will be formed, however, by the reaction of HO2 radicals with NO. The fraction \( f_{sc} \) was determined from the yields of butanal, using an estimate of 0.036 for the ratio \( k_{8b}/k_{8a} \) and an estimate of 0.29 for the ratio \( k_{8a}/k_{8c} \) based on estimated rate constants (1), \( f_{sc} = 13 \pm 3 \). The fraction \( f_{sc} \) can also be derived from the yields of ethanal, \( f_{sc} = 18 \pm 3 \). The fraction \( f_{sc} \) determined from the yields of butanal is based on the assumption that reaction 9b is unimportant, which is indicated by estimated rate constants (1). As we observed the formation of methanal (from reaction 9b) and propanal (proposed to be formed from the n-propyl radical formed in reaction 9b), this could indicate either an incorrect estimation method or additional sources of these compounds not considered in the proposed mechanism. However, the two values derived for \( f_{sc} \) do agree within the experimental errors.

The fraction of 2-hexoxy radicals reacting by 1,5-H shift isomerization can be calculated from the yields of 5-hy-
TABLE 2
Summary of Results

<table>
<thead>
<tr>
<th>Channel</th>
<th>Process</th>
<th>Product Yields Used for Calculation</th>
<th>Hexyl Nitrite Photolysis Exp$^a$</th>
<th>Hexane + OH Exp$^d$</th>
<th>Estimate$^e$</th>
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<tr>
<td>f$_{2a}$</td>
<td>+ O$_2$</td>
<td>hexan-2-one</td>
<td>2 ± 1</td>
<td>0.8 ± 0.5</td>
<td>0.3</td>
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<tr>
<td>f$_{2b}$</td>
<td>Δ</td>
<td>pentanal</td>
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<td>0</td>
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<tr>
<td>f$_{2c}$</td>
<td>Δ</td>
<td>butanal</td>
<td>13 ± 3</td>
<td>0.6 ± 0.2$^a$</td>
<td>0</td>
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<tr>
<td>f$_{2d}$</td>
<td>1,5-H shift</td>
<td>5-OH-hex-2-one$^f$</td>
<td>68 ± 48</td>
<td>98 ± 30</td>
<td>99.7</td>
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<tr>
<td>f$_{2e}$</td>
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<tr>
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<td>83 ± 52</td>
<td>98 ± 30</td>
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2-Hexoxy Radicals

3-Hexoxy Radicals

<table>
<thead>
<tr>
<th>Channel</th>
<th>Process</th>
<th>Product Yields Used for Calculation</th>
<th>Hexyl Nitrite Photolysis Exp$^a$</th>
<th>Hexane + OH Exp$^d$</th>
<th>Estimate$^e$</th>
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<tbody>
<tr>
<td>f$_{3a}$</td>
<td>+ O$_2$</td>
<td>hexan-3-one</td>
<td>15 ± 5</td>
<td>7 ± 4</td>
<td>21.1</td>
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<tr>
<td>f$_{3b}$</td>
<td>Δ</td>
<td>butanal</td>
<td>6 ± 1</td>
<td>7 ± 5</td>
<td>2.5</td>
</tr>
<tr>
<td>f$_{3c}$</td>
<td>Δ</td>
<td>propanal</td>
<td>10 ± 2</td>
<td>9 ± 3</td>
<td>2.5</td>
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<tr>
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<td>77$^h$</td>
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<td>1.9</td>
</tr>
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</table>

$^a$ See Figures 1 and 3 and text. $^b$ Error limits are two least-squares standard deviations. $^c$ No correction for secondary OH radical attack applied. $^d$ Correction for secondary OH radical attack applied. $^e$ Based on estimated rate coefficients as given by Atkinson (1). $^f$ Calculated from the yield of 5-hydroxyhexan-2-one. $^g$ Calculation based on the yield of n-butyl nitrate using an estimate for the fraction leading to n-butyl nitrate (28). $^h$ Calculated by difference.

In an attempt to estimate the OH radical concentration in the reaction mixture, a separate experiment was conducted. Methanol (40 ppmv) was added to a mixture of 2-hexyl nitrite and NO in synthetic air prepared as described above containing reactant concentrations of the same order as in runs 1–3. During the irradiation, the decay of methanol was monitored using GC/FID. Methanol was chosen as it gives rise only to the formation of methanal and HO$_2$ radicals (26). The HO$_2$ radicals will react with NO to reform the OH radicals. Using the known rate coefficient for the reaction of methanol with OH radicals (27), the OH radical concentration could be calculated according to the rate expression for the decay of methanol. The concentration of OH radicals was found to be in the order of 8 × 10$^9$ molecules cm$^{-3}$. This value is affected with a large uncertainty owing to the inaccuracies in the determination of the methanol concentration. We also assumed the OH radical concentration to be constant.

To estimate the contribution to the yields of aldehydes from the photooxidation of the hexyl nitrite, the rate coefficient for the reaction of 2-hexyl nitrite with OH radicals was extrapolated from measured rate coefficients for a series of alkyl nitrites (28), and a hypothetical mechanism for the photooxidation of 2-hexyl nitrite was derived according to the general reaction scheme presented above. The product distribution was calculated using estimated rate coefficients as given by Atkinson (1). The contribution to the yields of ethanal and butanal from the reaction of OH radicals with hexyl nitrite is estimated to be 5% at most. Therefore, this mechanism cannot fully explain the high yields of ethanal and butanal measured, but it accounts for the propanal observed. The rate coefficient for the reaction of OH radicals with 5-hydroxyhexan-2-one was estimated by the procedures of Atkinson (24) to be 1.1 × 10$^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 298 K. The loss of 5-hydroxyhexan-2-one due to secondary OH radical attack was then estimated, but this estimate fell considerably short of the observed loss of this compound. Furthermore, the observed yields of hexan-2,5-dione do not completely account for the estimated loss.
FIGURE 3. Schematic representation of the reactions of the 3-hexoxy radical under tropospheric conditions. The observed products are drawn in boxes.

of 5-hydroxyhexan-2-one due to reaction with OH radicals, which may reflect an error in the estimated OH radical concentration.

We also considered other possible loss processes for 5-hydroxyhexan-2-one. A gas mixture of synthetic air and that compound was prepared in the bag reactor. There was no evidence for loss to the wall of the reactor. The mixture was also irradiated using the black lamps for 4 h, and only a very small decay of 5-hydroxyhexan-2-one was observed. This effect cannot account for the high losses observed on the time scale of the alkyl nitrite photolysis experiments.

As we detected several furans by GC/MS, we also have to consider if these compounds could be formed from the hydroxy ketone. For example, hexan-2,5-dione can form 2,5-dimethylfuran in the presence of a catalyst at elevated temperatures (29). In a similar way, 5-hydroxyhexan-2-one could form 2,3-dihydro-2,5-dimethylfuran. Tests have been conducted to identify the sources of the observed furans, but the results were inconclusive, and it is not possible to confirm or rule out the gas-phase formation of the furans. It could also be possible that the furans are formed from the alkoxy radicals directly, although the mechanisms of such reactions are not obvious.

The large error limits in derived from the alkyl nitrite photolysis experiment probably reflect the problems of determining the fractions due to the unaccountable loss processes of 5-hydroxyhexan-2-one.

3-Hexoxy Radical Reactions from Photolysis of 3-Hexyl Nitrite. The photolysis of 3-hexyl nitrite is assumed to occur mainly via the homolytic cleavage of the RO—NO bond (23) as shown for 2-hexyl nitrite in reaction 5. According to the general reaction scheme proposed, the 3-hexoxy radical may react with $O_2$ (reaction 19a), decompose (reactions 19b and 19c), isomerize by 1,5-H shift (reaction 19d), or isomerize by 1,4-H shift (reaction 19e) (see Figure 3).

The ethyl radical formed in reaction 19b is thought to yield ethanal (reaction channel 20) (30). The propyl radical formed in reaction 19c is thought to yield propanal (reaction channel 21) (1). The 4-hydroxy-1-hexyl radical formed by 1,5-H shift isomerization (reaction 19d) is thought to react analogously to the 5-hydroxy-2-hexyl radical described above. The 4-hydroxy-2-hexyl radical formed by 1,4-H shift isomerization (reaction 19e) would be expected to react in the same way as the 5-hydroxy-2-hexyl radical as described above.

The observed products and their proposed reaction sources were as follows: hexan-3-one formed in reaction 19a, butanal formed in reaction 19b, ethanol from the ethyl radical formed in reaction 19b, and propanal formed in reaction 19c and from the propyl radical also formed in reaction 19c.

The fractions of 3-hexoxy radicals proceeding through reactions 19a–19c were derived as described for the 2-hexoxy radicals. A summary of the results is shown in Table 2.

Ethyl radicals (formed in reaction 19b) will form ethanal uniquely (30), and hence the fraction proceeding through channel $f_{eb}$ can be calculated from the yield of ethanal, $f_{eb} = 24 \pm 7\%$. This value is significantly higher than the value derived from the butanal yields, which probably indicates additional sources of ethanal. Propyl radicals are proposed to form propanal uniquely (1). The fraction proceeding through channel $f_{eb}$ can then be found from the yields of propanal allowing for the two sources of this compound. The 4-hydroxy-1-hexyl radical formed by 1,5-H shift isomerization (reaction 19d) would be expected to yield the stable products 6-nitrooxyhexan-3-ol and 6-hydroxyhexan-3-one. Authentic samples of these compounds were not available, and consequently we were unable to clearly identify these products. However, we believe the unknown compound observed both in the hexane photolysis and the 3-hexyl nitrite photolysis could be 6-hydroxyhexan-3-one, as this compound was not observed in the 2-hexyl nitrite experiments and as the qualitative concentration profile shows a similar pattern to that for 5-hydroxyhexan-2-one. Owing to this lack of
product identification and quantification, the fraction of 3-hexoxy radicals undergoing 1,5-H shift isomerization cannot be determined directly. The 4-hydroxy-2-hexyl radical formed by 1,4-H shift isomerization (reaction 19e) would be expected to react to yield 5-hydroxyhexan-2-one and 5-nitroxyhexan-2-ol. Authentic samples of these compounds were unobtainable, but we could find no indications of such possible products in our analyses and consequently we believe that $f_{19e} = 0$. The fraction of 3-hexoxy radicals reacting by 1,5-H shift isomerization was calculated by difference using the value for $f_{19a}$ derived from the butanal yields, i.e., $f_{19a} = 1 - f_{19a} - f_{19b} - f_{19c}$.

**OH Radical-Initiated Photooxidation of Hexane.** The photolysis of nitrous acid leads to the formation of hydroxyl radicals (9). Hydroxyl radicals may abstract a hydrogen atom from one of the primary or secondary carbon atoms in hexane. Since abstraction of a secondary hydrogen atom is estimated to occur 95% of the time (24), the reactions following the abstraction of a primary hydrogen atom will be neglected here.

Abstraction of a secondary hydrogen atom by OH radicals can occur from two different secondary carbon atoms. The alkyl radicals formed will then add oxygen to form alkyl peroxy radicals. The reaction rates of the individual steps leading to the generation of alkyl peroxy radicals are unknown. However, we will assume that equal amounts of each peroxy radical isomer are generated. The alkyl peroxy radicals will then react with NO to form either the alkoxy radicals (reactions 22a and 23a) or the alkyl nitrates (reactions 22b and 23b).

\[
\begin{align*}
\text{CH}_3\text{CH(OO)}(\text{CH}_2)_3\text{CH}_3 + \text{NO} &\rightarrow \\
\quad \text{CH}_3\text{CH(O)}(\text{CH}_2)_3\text{CH}_3 + \text{NO}_2 &\quad \text{(22a)}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH(OO)}(\text{CH}_2)_3\text{CH}_3 + \text{NO} + \text{M} &\rightarrow \\
\quad \text{CH}_3\text{CH(ONO)}(\text{CH}_2)_3\text{CH}_3 + \text{M} &\quad \text{(22b)}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH(OO)}(\text{CH}_2)_2\text{CH}_3 + \text{NO} &\rightarrow \\
\quad \text{CH}_3\text{CH}_2\text{CH(O)}(\text{CH}_2)_2\text{CH}_3 + \text{NO}_2 &\quad \text{(23a)}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH(OO)}(\text{CH}_2)_2\text{CH}_3 + \text{NO} + \text{M} &\rightarrow \\
\quad \text{CH}_3\text{CH}_2\text{CH(ONO)}(\text{CH}_2)_2\text{CH}_3 + \text{M} &\quad \text{(23b)}
\end{align*}
\]

The possibility of self-reactions of the RO2 radicals in this study is discounted in the presence of the relatively high concentrations of NO. Based on the yields of 2-hexyl nitrate and 3-hexyl nitrate, the fractions proceeding through reactions 22b and 23b were found to be 11 ± 3% and 9 ± 2%, respectively. The sum of the alkyl nitrates formed is in very good agreement with the value derived by Atkinson et al. (31), which was determined to be 20.8 ± 2.7%. The values for the alkyl nitrate isomers ratio [3-hexyl nitrate]/[2-hexyl nitrate] do not agree, 0.78 ± 0.29 in this study to 1.34 ± 0.11 (31). The reason for this discrepancy is not known. The 2-hexoxy radical formed in reaction 22a and the 3-hexoxy radical formed in reaction 23a are proposed to react as described above for the alkoxy radicals generated from the hexyl nitrate photolysis and are discussed in relation to Figures 1 and 3.

The formation of 5-nitroxyhexan-2-ol (reaction 14b) was observed, although reliable quantification was not possible. This is probably due to irreversible adsorption on sampling lines or in the chromatographic apparatus (32). Nitrate formation from a 3-hydroxyalkyl peroxy radical has been suggested to be negligible (2). The formation of the nitrate is an important finding with regard to the chemistry of polluted air, since through this reaction both NO and peroxy radicals are removed from the system. Using the maximum concentration of 5-nitroxyhexan-2-ol observed, which includes the estimate for the amount adsorbed on the walls of the bag reactor (see results section), we determined the upper limit of the ratio $k_{14b}/k_{14a}$ to be 0.09.

For a quantitative assessment of the importance of each reaction channel for the reactions of the hexoxy radicals, the observed yields of the primary products were corrected for secondary OH radical attack, and the fractions were calculated as described by Atkinson et al. (31) and Eberhard et al. (9). For the correction of the yields of 5-hydroxyhexan-2-one, the rate coefficient for the reaction with OH radicals was estimated using the procedure by Atkinson (24). For all other products, the rate coefficients were taken from Atkinson (33) or from Atkinson et al. (27). The derived fractions are presented in Table 2. In the absence of known light intensities in these experiments, we did not correct for secondary photolyses of any of the carbonyl products in the hexane system, but these should not be major loss processes.

The fraction $f_{3a}$ was derived from the yield of n-butyl nitrate using the estimate of 0.036 for the ratio $k_{3a}/k_{8a}$ (25). Based on the yields of 5-hydroxyhexan-2-one, $f_{3a}$ was derived using the upper limit of 0.09 for the ratio $k_{3a}/k_{14a}$. In these experiments, we did not observe the pronounced decay in the concentration of 5-hydroxyhexan-2-one as found in the hexyl nitrate photolyses. We did not find evidence for the occurrence of 1,4-H shift isomerization of the 2-hexoxy radicals, i.e., $f_{3a} = 0$.

The fractions $f_{19b}$ and $f_{19c}$ were calculated from the yields of butanal and propanal, respectively. These aldehydes were assumed to be unique products, the contributions from the reaction channels following the formation of the n-butoxy radical have been omitted owing to the very low observed yield of n-butyl nitrate (and hence small value of $f_{3a}$). $f_{3a}$ was calculated by difference assuming that no 1,4-H shift isomerization occurs and we did not find evidence for the occurrence of that process, $f_{3a} = 1 - f_{19a} - f_{19b} - f_{19c}$ and $f_{3a} = 0$.

The yields of hexan-2,5-dione are greater than the calculated loss of 5-hydroxyhexan-2-one by OH radical attack at the tertiary carbon atom. This could indicate either that the rate constant for 5-hydroxyhexan-2-one with OH radicals is underestimated by the method of Atkinson (24) or that some of the 5-hydroxyhexan-2-one is lost by an unknown process (see discussion for the hexyl nitrate photolysis experiment). However, in this case the loss is much less pronounced than in the case of the alkyl nitrate photolysis experiment.

**Comparison of Results from Different Hexoxy Radical Sources.** The two experimental values of the fraction of 2-hexoxy radicals reacting with oxygen ($f_{3a}$) agree within the experimental errors. Pentanal could not be found in any of the experiments confirming that $f_{3a} = 0$. The two experimental values of $f_{3a}$ are significantly different. The reasons for the disagreement could include (i) an error in the determination of the the n-butyl nitrate yield, the concentrations being in the order of 30–200 pptv, and (ii) additional sources for butanal and ethanol not accounted for in the proposed mechanism such as photooxidation of the hexyl nitrate initiated by OH radical attack. Although
the hexyl nitrite is present in relatively high concentrations, as discussed in the section on 2-hexoxy radicals from the hexyl nitrite photolyses, our estimates of the contribution to aldehydes from this source, based on assumed photooxidation mechanisms and estimated rate coefficients, only amounted to about 5%. As both \( f_{ba} \) and \( f_{c} \) are higher in the hexyl nitrite experiments than in the hexane experiments, they could also indicate an underestimation of the hexyl nitrite loss.

Within the experimental errors, the values of \( f_{ba} \) derived directly are in agreement. The lower value derived from the hexyl nitrite experiment is probably caused by difficulties associated with unaccountable loss processes of 5-hydroxyhexan-2-one. It is tempting to conclude that the discrepancies in measuring the 5-hydroxyhexan-2-one in the 2-hexyl nitrite experiments arise from the much higher conversions in these experiments, ~60%, as opposed to the hexane experiments, ~20% (see Table 1). As discussed in the section on the 2-hexoxy radicals from the photolysis of 2-hexyl nitrite, however, our estimates of the secondary attack on 5-hydroxyhexan-2-one fell considerably below the observed loss of this compound. This result is, however, critically dependent upon the highly uncertain estimate of the OH radical concentration.

The two experimental values of the fraction of 3-hexoxy radicals reacting with oxygen \( (f_{ba}) \) agree within the experimental errors. The fractions \( f_{1b}, f_{3c}, \) and \( f_{0d} \) are in good agreement.

**Comparison of Present Results with Predictions.** The fractions derived can be compared to predictions based on rate coefficients estimated using the procedures given by Atkinson (1). The estimated values are also given in Table 2. The value estimated for \( f_{ba} \) is lower than the values derived from the measurements. The lack of pentanal formation \( (f_{ba}) \) is in agreement with the prediction. There is a significant discrepancy for \( f_{sc} \), which is estimated to be zero. The high yields of ethanal and butanal observed in the nitrite photolysis experiments could indicate either an incorrect estimation or additional sources for these compounds not accounted for in the reaction mechanism. This could be explained by OH radical attack on 2-hexyl nitrite. The measured fraction of 2-hexoxy radicals undergoing 1,5-H shift isomerization \( (f_{ba}) \) is the same as that estimated. In the case of the hexyl nitrite photolysis experiment, the lower value could be caused by the problems associated with the determination of the fraction due to loss processes for 5-hydroxyhexan-2-one. We did not find evidence for the occurrence of 1,4-H shift isomerization \( (f_{ba}) \), which is in agreement with the prediction.

The predicted fraction of 3-hexoxy radicals reacting with \( O_2 \) is higher than the values derived from the measurements. Both \( f_{3c} \) and \( f_{sc} \) are higher than predicted. The reasons for the disagreement could include (i) errors in estimation, (ii) additional sources for butanal and propanal not accounted for in the proposed mechanism such as photooxidation of the hexyl nitrite initiated by OH radical attack, (iii) in the case of the hexane photooxidation experiment, an incorrect determination of the \( n \)-butyl nitrate yield leading to a low value for \( f_{ba} \), i.e., an underestimation of the sources of butanal and propanal from the reactions following reaction 6c. The fraction of 3-hexoxy radicals undergoing 1,5-H shift isomerization calculated by difference is in good agreement with the prediction, but the small predicted fraction of isomerization via 1,4-H shift could not be confirmed by the experiments.

**Comparison of Present Results with Literature Data.** The present study does not yield an absolute rate coefficient of the isomerization of hexoxy radicals, but indicates that under atmospheric conditions a large fraction of the radicals (~68%) isomerize rather than decompose or react with oxygen. In this regard, our approximate quantitative data are in line with the thermochemical kinetic estimates \( (1) \) of the rate coefficients of the isomerization \( (k_{iso}) \) of such radicals, e.g., for 2-hexoxy (1,5-H shift with \(-CH_2-\) group), \( k_{iso} = 1.5 \times 10^5 \text{ s}^{-1} \) and for 3-hexoxy (1,5-H shift with \(-CH_3\) group), \( k_{iso} = 1.3 \times 10^5 \text{ s}^{-1} \).

On the other hand, Dóbé et al. (7) reported a value of \( k_{iso} = 1.4 \times 10^4 \text{ s}^{-1} \) for the 2-pentoxy radical (1,5-H shift with \(-CH_3\) group), about a factor of 10 lower than the estimates. Doubts have been expressed \( (1) \) on the validity of the Dóbé et al. (7) results for the 2-pentoxy radical on the grounds of possible difficulties in quantitatively monitoring the end products of the isomerization reaction. Certainly the concentration of \( CH_3 \) radicals used to trap the isomerized radical in the Dóbé et al. (7) system was considerably less than the concentration of \( O_2 \) in the present experiments.

**Conclusions.** We have observed for the first time products from the isomerization reactions of hexoxy radicals produced under conditions relevant to the atmosphere directly from hexyl nitrite photolyses or from the OH radical-initiated photooxidation of hexane. The fractions of 2- and 3-hexoxy radicals isomerizing, as opposed to reacting with oxygen or thermally decomposing, are high (~68%). Though the analytical complexities of the experimental systems are such that precise data were not obtained, the approximate quantitative data are in accord with calculations of the fractions of the alkoxy radicals based on kinetic and thermochemical estimates of the rate coefficients of the alkoxy radical reactions.

**Implications for Atmospheric Chemistry.** The results show that 1,5-H shift isomerization is the dominant reaction process for longer chain alkoxy radicals. The predictions are in fairly good agreement with the measurements. The estimation method by Atkinson is a valuable tool for predicting these reactions, but more experimental quantitative data are needed for the assessment of the fate of the \( \delta \)-hydroxy alkyl nitrates formed by 1,5-H shift isomerization. In this regard, it would be useful to obtain more quantitative information on the formation of the hydroxyalkyl nitrates from the reactions of the isomerized radicals with NO. This has important implications with regard to the radical inhibiting properties of alkanes (C ≥ 4) in NOx polluted atmospheres. The hydroxylated products observed in the present laboratory experiments should be observable in polluted air, although the bifunctional alkyl nitrates may be difficult to detect owing to their adsorptive properties.

**Note Added.** After the submission of this paper, we learned that Atkinson and Aschmann (34) have recently obtained direct evidence from product studies for the isomerization of the \((CH_3)_2CHCH_2C(O)CH_2C(O)CH_3\) radicals, generated in the photooxidation of 2,6-dimethylheptan-4-one in the presence of NOx.

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Literature Cited


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