Laboratory Studies of the OH-Initiated Photooxidation of Di-*n*-propyl Ether

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ABSTRACT: The OH-initiated photooxidation of di-*n*-propyl ether was investigated in this study. Di-*n*-propyl ether was mixed with nitric oxide and a hydroxyl radical precursor and irradiated using UV black lamps in a glass environmental chamber. Mass spectrometry was used as the primary analytical technique to monitor the reactants and products. FTIR spectroscopy was used to monitor formaldehyde. The products observed were propyl formate, acetaldehyde, propionaldehyde, and propyl propionate, with molar yields relative to di-*n*-propyl ether concentration loss of 0.61 \pm 0.044, 0.60 \pm 0.057, 0.15 \pm 0.062, and 0.043 \pm 0.015, respectively. Errors represent $\pm 2\sigma$. Nitrates could not be quantified because of a lack of commercially available standards. However, evidence exists for nitrate formation from the photooxidation of di-*n*-propyl ether. Formaldehyde concentrations were negligible.

Mechanism predictions were performed on the di-*n*-propyl ether/OH system using the Carter kinetic software. Propyl formate and acetaldehyde yields were reasonably predicted (under 11.7% error). However, propionaldehyde and propyl propionate yields were vastly underpredicted, and examination of the experimental data suggested secondary production of both propionaldehyde and propyl propionate. Reactions were proposed for the photolysis and OHinitiated photooxidation of a primary nitrate product (1-propoxy propyl nitrate) that resulted in the formation of propionaldehyde and propyl propionate. Basic semiempirical computational chemistry calculations at the UHF/PM3 level of theory were performed using Hyperchem® to investigate pathways for the secondary formation of propionaldehyde in particular. © 2000 John Wiley & Sons, Inc. Int J Chem Kinet 32: 703–711, 2000

INTRODUCTION

Ethers are currently used as industrial solvents and as fuel additives. Oxygenated compounds such as methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE) are added to gasoline to increase the octane number and reduce the production of CO [1]. In past years, compounds such as di-isopropyl ether (DIPE)

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and *tert*-amyl methyl ether (TAME) were proposed for use in automotive fuels [2].

Due to the high volatility of ethers, evaporation into the troposphere is not uncommon. Given the increased use of ethers in new fuels and in combustion processes, it is important to assess the impact of these compounds on the atmosphere. Investigations into the atmospheric kinetics and mechanisms of ethers such as MTBE, ETBE, and DIPE with .OH radicals have already been published [3-6]. In general, the mechanisms of hydroxyl attack on ethers and the reactivity of alkoxy radicals derived from ethers are not well

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understood. Atkinson [7] has remarked that alkoxy radicals produced from hydroxyl/ether reactions have reaction rates that cannot currently be accurately predicted. Additional work is clearly required.

Ethers are degraded in the atmosphere predominately by hydroxyl radical reaction [8]. Removal by photolysis and reaction with ozone is considered slow enough to be negligible [9,10]. The hydroxyl radical reaction with ethers proceeds via abstraction of a hydrogen atom from --CH-, --CH₂-, or --CH₃ groups. Previous studies of ethers have suggested that the oxygen in ethers has a long-range activating effect on the hydrocarbon chain [11-15]. Ethers display $-CH_2$ group reactivities approximately three times higher than $-CH_2$ groups in alkanes [11]. This inductive effect appears to decrease after the delta or epsilon carbon. After this point, the reactivities of $-CH_2$ groups in ethers become indistinguishable from those of $-CH_2$ groups in alkanes. The activating effects for oxygen observed in previous studies are not expected from either thermochemical data or inductive effects [13]. Nelson has suggested that the increased reactivity must be due to other undetermined mechanistic issues [13].

Previous studies of di-*n*-propyl ether have focused on the kinetics of the \cdot OH-initiated reaction [11,13,16,17]. To date, product studies on this compound have not been reported in the literature. Product studies of similar ethers such as di-methyl ether and di-ethyl ether have been reported in the literature [3,18,19]. The study performed at the University of Florida serves to expand the available database of reaction mechanisms of ethers.

EXPERIMENTAL METHODS

The reactions of di-*n*-propyl ether were conducted in a 213-L borosilicate glass chamber that was custommanufactured by Infrared Analysis Inc. (Anaheim, CA). Gas-phase reactants were introduced into the chamber using a glass manifold system, which consisted of a calibrated 1.87-L glass bulb and MKS Baratron pressure gauges (MKS Inc.). Boyle's law was used to calculate the concentrations in parts per million by volume. Dry, zero air (Strate Welding Inc.) was used to flush the reactants into the chamber, and acted as the diluent. Mixing was achieved using an internal brushless Teflon[®]-coated mixing fan (Infrared Analysis, Inc.). A schematic of the system appears in Figure 1.

Photolysis reactions were initiated by 14 UV lamps (GE F40BL). The lamps were mounted on a cylindrical surface around the chamber and were surrounded by a custom-designed metal reflector to maximize



Figure 1 Diagram of the reaction chamber system.

light intensity within the chamber. The rate constant of NO₂ photolysis in the presence of N₂ was used as a measure of the lamp intensity and was determined to be approximately 0.5 min⁻¹. Two black drapes covered the chamber to prevent outside light from entering the chamber. All experiments were carried out at room temperature (298 \pm 2 K) and at 760 Torr.

Gas samples from the experiments were analyzed primarily using a Finnigan MAT GCQ[®] system (Model 9001 gas chromatograph coupled to a mass spectral detector). The samples were drawn into a nickel sample loop (ca. 1 ml) and were injected onto a J&W Scientific DB-WAX GC column (0.25 mm × 30 m × 0.25 μ m) using a heated 6-port variable restrictor metering valve. The GC temperature program used was: 35°C for 5 min. followed by a ramp of 10°C/min. to a final temperature of 150°C. Ultra-high-purity helium (BITEC, Inc.) was used as the carrier gas. Mass spectral analyses were performed in electron ionization mode.

The contents of the chamber were also analyzed *in situ* using a Fourier transform infrared (FTIR) spectrometer (Model M, MIDAC, Inc.). The MIDAC instrument initiated an IR beam that was directed into the chamber through a 3-in. diameter, 3-mm thick KCl transmission window (International Crystal). The beam was reflected multiple times inside the chamber using two opposite-facing silver-coated mirrors, which were custom-manufactured by Infrared Analysis, Inc. (Figure 1 only illustrates four passes of the IR beam used in infrared detection and analysis.) The IR beam

exited through a 3-in. diameter, 3-mm thick KCl transmission window and was collected by an external MCT detector. The path length used for these studies was 144 m, achieved by making 48 passes through the 3-m-long chamber. The minimum and maximum achievable path lengths were 6 m and 360 m, respectively. Experiments were performed with an IR resolution of 0.5 cm⁻¹ and a scan range of 3000 to 500 cm⁻¹. Infrared spectra were developed by coadding 16 interferogram scans.

Hydroxyl radicals were generated from the photolysis of methyl or ethyl nitrite in air containing NO. The mechanism is as follows:

$$\operatorname{RCH}_2\operatorname{ONO} + h\nu \longrightarrow \operatorname{RCH}_2\operatorname{O} \cdot + \operatorname{NO} \quad (1)$$

$$\operatorname{RCH}_2\operatorname{O} \cdot + \operatorname{O}_2 \longrightarrow \operatorname{RCHO} + \operatorname{HO}_2 \cdot \qquad (2)$$

$$HO_2 \cdot + NO \longrightarrow \cdot OH + NO_2$$
 (3)

where R represents H for methyl nitrite and CH_3 for ethyl nitrite.

When methyl nitrite is used to generate \cdot OH radicals, formaldehyde is also produced. Since formaldehyde is a potential product of di-*n*-propyl ether photoxidation, experiments were performed with ethyl nitrite as the source of \cdot OH radicals to specifically search for formaldehyde as a product. In such experiments, ethyl nitrite produces acetaldehyde instead of formaldehyde.

Both hydroxyl radical precursors were prepared in gram quantities using the method of Taylor et al. [20]. Methyl nitrite was stored at room temperature in a stainless steel lecture bottle while ethyl nitrite was stored at -80° C in a glass vial. The purity of methyl and ethyl nitrite was verified by FTIR, and no contaminants were detected.

The product study consisted of placing di-n-propyl ether, the hydroxyl radical precursor, and nitric oxide in the chamber, photolyzing the mixture, and monitoring changes in reactant and product concentrations over time. Typical starting concentrations for the reactants were 26-28 ppm of di-n-propyl ether, 41-43 ppm of methyl nitrite, and 19-20 ppm of NO. The concentrations used for ethyl nitrite experiments were 10-11 ppm of di-n-propyl ether, 13-14 ppm of ethyl nitrite, and 7-8 ppm of NO. Sampling consisted of taking three time-zero samples for GC-MS analyses, turning on the UV lamps for 30-60 s intervals, and then taking two duplicate samples for GC-MS analyses after each successive photolysis. (In the experiments with ethyl nitrite, each GC-MS analysis was followed by an FTIR analysis.) Total photolysis times were between 4 and 5 min for each experiment. The duplicate samples taken after each photolysis were

compared with each other to confirm that reactions had halted. Indeed, given the excellent agreement (3%) between duplicate samples analyzed via GC-MS for a single photolysis event, the reactions had halted.

Separate studies were conducted using the GC-MS on di-*n*-propyl ether and the products to determine the extent of loss via photolysis and to the walls. All studies indicated negligible (<5% total) decrease in concentrations over time scales typical of those used in the product studies. Aldehyde and ester loss due to photolysis was not observed in the given experimental system, as expected from consideration of absorption cross section data [9].

Because of the ease in separating multicomponent systems via GC, product peaks were identified by GC-MS analysis using retention times and mass spectra. The FTIR spectrometer was used only to quantify formaldehyde. Product concentrations were determined from GC-MS analysis by using standards to find peak area/concentration ratios. Formaldehyde concentrations were determined from laboratory-calibrated FTIR reference spectra available in our standard reference library. Di-*n*-propyl ether (Aldrich, 99^+ %). propyl formate (Aldrich, 97%), propionaldehyde (Aldrich, 97%), propyl propionate (Aldrich, 99%), and acetaldehyde (Aldrich 99.5+%) were obtained commercially and were further vacuum purified before use. Product molar yields per reactant concentration loss were determined from a linear least-squares fit of the product concentrations plotted versus the amount of reacted di-n-propyl ether.

RESULTS

The products of the ·OH-initiated photooxidation of di-n-propyl ether were propyl formate (HC(O) $OC_{3}H_{7}$), acetaldehyde (CH₃CHO), propionaldehyde (CH₃CH₂CHO), and propyl propionate (CH₃CH₂C(O) OCH₂CH₂CH₃). А exhibited peak that characteristics of a nitrate (i.e., it contained a strong fragment at m/z = 46) was also observed in the chromatograms. Unfortunately, though, commercial samples of the nitrate were not available for comparison; thus, a positive identification could not be ascertained. However, the subject of nitrate formation will be discussed subsequently. A typical post-photolysis chromatogram is given in Figure 2 and illustrates that most of the products were observable by GC-MS analysis. As stated previously, since the GC-MS technique provided for easier separation and detection of compounds, it was used as the primary analytical technique. In the figure, the terms TOT, 41, 43, and 57 in the individual frames refer to the fragment ions that were scanned in that frame. The term TOT, or Total



Figure 2 Chromatogram of a chamber sample after 300 s total of photolysis. Compounds detected include (1) di*-n*-propyl ether, (2) propyl formate, (3) acetaldehyde, (4) propionaldehyde, (5) unidentified nitrate, (6) propyl propionate, and (7) air.

Ion Count, indicates that all of the ion fragments within the measured mass-to-charge ratio range of 34–120 were scanned.

The product concentrations were corrected for secondary hydroxyl radical reaction (reactions of products with hydroxyl radicals) using the correction factor, *F* [21]:

$$F = \frac{\frac{(k_1 - k_2)}{k_1} \times \left(1 - \frac{(\text{test compound})_t}{(\text{test compound})_0}\right)}{\left(\left(\frac{(\text{test compound})_t}{(\text{test compound})_0}\right)^{k_1/k_2} - \frac{(\text{test compound})_t}{(\text{test compound})_0}\right)}$$
(4)

where k_1 and k_2 are rate constants for the test compound (di-*n*-propyl ether) and product compound, re-

spectively. The subscripts t and 0 refer to samples taken at time t and time zero, respectively. Rate constants for the observed products are given in Table I. The calculated correction factor ranges for propyl formate, acetaldehyde, propionaldehyde, and propyl propionate were 1.00-1.03, 1.03-1.25, 1.03-1.34, and 1.01-1.06, respectively. The raw concentrations determined from experiments were multiplied by the correction factor to obtain corrected yields.

Additional experiments were performed to examine secondary sources of the observed products. Each commercially available product was placed in the chamber with methyl nitrite and NO and was photolyzed for times comparable to those used in the original product study. GC-MS analyses revealed no secondary sources of propyl formate, propionaldehyde, or propyl propionate from the compounds tested. However, acetaldehyde was produced from •OH reactions with propionaldehyde and propyl propionate. The acetaldehyde concentrations measured in the di-*n*-propyl ether experiments were therefore corrected to take these secondary sources into account.

Plots of the corrected product concentration data versus the change in di-*n*-propyl ether concentrations appear in Figure 3. Linear least-squares fit of the data were used to obtain molar yields for the products. These yields were 0.61 ± 0.044 for propyl formate, 0.60 ± 0.057 for acetaldehyde, 0.15 ± 0.062 for propionaldehyde, and 0.043 ± 0.015 for propyl propionate. Quoted errors represent $\pm 2\sigma$. It is important to note the curvature in the propionaldehyde and propyl propionate data in Figure 3B. This curvature contributed to the relatively large errors in the yields for propionaldehyde and propyl propionate, and is indicative of secondary formation of these products, as will be discussed subsequently.

FTIR analysis of the ethyl nitrite/di-*n*-propyl ether experiments was used solely for the detection and quantification of formaldehyde. Formaldehyde was quantified using an FTIR spectral range of 2769-2765cm⁻¹. Formaldehyde production from di-*n*-propyl ether/·OH reactions was negligible.

The observed products account for approximately 73% of the carbon from the reacted di-*n*-propyl ether. It is possible that nitrates or isomerization products

 Table I
 Rate Constants for Product/•OH reactions

Products	$k imes 10^{12} m cm^3 m molecule^{-1} m s^{-1}$	Source
Proply formate	2.38 ± 0.27 @ 296	Wallington et al.[22]
Acetaldehyde	$16.2 \pm 1.0 @ 298$	Scollard et al. [23]
Propionaldehyde	$22.2 \pm 0.9 @ 298 \pm 2$	Niki et al. [24]
Propyl propionate	4.02 ± 0.32 @ 296	Wallington et al. [22]



Figure 3 (A) Plots of propyl formate (\times) and acetaldehyde (\Box) concentrations versus the change in di-*n*-propyl ether concentration. The dotted and solid lines represents linear least squares fit of the propyl formate and acetaldehyde data, respectively. (B) Plots of propyl propionate (\bigcirc) and propionaldehyde (\times) concentration versus the change in di-*n*-propyl ether concentration. The solid lines represent linear least-square fits to the data. The dotted lines are presented to show the curvature in the propyl propionate and propionaldehyde data.

were formed in the chamber that were not observed or could not be quantified. Losses of these products to the chamber walls and GC/MS equipment were also possible. However, standard samples were not available to confirm these possibilities.

DISCUSSION

The probabilities for hydroxyl radical attack on each of di-*n*-propyl ether's six carbon sites were determined using the structure activity relationship (SAR) [25]. Based on experimental data, the SAR is used to predict rate constants for organic reactions with •OH radicals by assigning a reactivity to each carbon in a hydrocarbon chain and then adding these reactivities to pro-

duce the overall rate constant. The probability of attack at each carbon site is determined by dividing each carbon's reactivity by the overall rate constant. The SAR method suggested the most likely site of hydroxyl radical attack on di-*n*-propyl ether was on the secondary carbon at site III:



with a total probability of 88.0%. The probability of attack on the remaining sites were 10.5% and 1.50% for sites II and I, respectively.

Using the SAR, the most likely site of \cdot OH attack on di-*n*-propyl ether is at carbon site III. Hydrogen abstraction at this site forms a radical (reaction 5) that can then react with O₂ (reaction 6) to form a peroxy radical. This peroxy radical can then react with NO to produce either an alkoxy radical (reaction 7) or 1-propoxypropyl nitrate (reaction 8).

$$CH_{3}CH_{2}CH_{2}OCH_{2}CH_{2}CH_{3} + \cdot OH \longrightarrow$$
$$CH_{3}CH_{2}C \cdot HOCH_{2}CH_{2}CH_{3} \quad (5)$$

$$CH_{3}CH_{2}C \cdot HOCH_{2}CH_{2}CH_{3} + O_{2} \longrightarrow CH_{3}CH_{2}CH_{0}2 \cdot OCH_{2}CH_{2}CH_{3} \quad (6)$$

$$CH_{3}CH_{2}CH(O_{2} \cdot)OCH_{2}CH_{2}CH_{3} + NO \longrightarrow CH_{3}CH_{2}CH(O \cdot)OCH_{2}CH_{2}CH_{3} + NO_{2}$$
(7)

$$CH_{3}CH_{2}CH(O_{2} \cdot)OCH_{2}CH_{2}CH_{3} + NO \longrightarrow CH_{3}CH_{2}CH(ONO_{2})OCH_{2}CH_{2}CH_{3} \quad (8)$$

The di-propoxy radical formed in reaction 7 will either react with O_2 (reaction 9), decompose at the C—C bond (reaction 10), decompose at the C—O bond (reaction 11), or undergo isomerization through 1,5-hydrogen atom abstraction (reaction 12):

$$CH_{3}CH_{2}CH(O \cdot)OCH_{2}CH_{2}CH_{3} + O_{2} \longrightarrow CH_{3}CH_{2}C(O)OCH_{2}CH_{2}CH_{3} + HO_{2} \cdot (9)$$

$$\begin{array}{c} CH_{3}CH_{2}CH(O \cdot)OCH_{2}CH_{2}CH_{3} \longrightarrow \\ CH_{3}C \cdot H_{2} + HC(O)OC_{3}H_{7} \quad (10) \end{array}$$

$$CH_{3}CH_{2}CH(O \cdot)OCH_{2}CH_{2}CH_{3} \longrightarrow CH_{3}CH_{2}CHO + CH_{3}CH_{2}CH_{2}O \cdot (11)$$

$$CH_{3}CH_{2}CH(O \cdot)OCH_{2}CH_{2}CH_{3} \longrightarrow CH_{3}CH_{2}CH(OH)OCH_{2}C \cdot HCH_{3}$$
(12)

The observed yield of propyl formate indicated that

decomposition via the C—C bond (reaction 10) was a major pathway. Propionaldehyde was formed from decomposition at the C—O bond (reaction 11) and also by the subsequent reaction of $CH_3CH_2CH_2O$ · with O₂. Propyl propionate was formed from reaction with O₂ (reaction 9). Products of the isomerization reaction were not observed. However, commercially available standards were not available for comparison.

Acetaldehyde is formed from further reaction of the ethyl radical produced in reaction 10:

$$CH_3C \cdot H_2 + O_2 \longrightarrow CH_3CH_2O_2 \cdot (13)$$

$$CH_3CH_2O_2 \cdot + NO + M \longrightarrow CH_3CH_2ONO_2 + M$$
 (14)

$$CH_3CH_2O_2$$
 · + NO \longrightarrow CH_3CH_2O · + NO₂ (15)

$$CH_3CH_2O \cdot \longrightarrow \cdot CH_3 + HCHO$$
 (16)

$$CH_3CH_2O \cdot + O_2 \longrightarrow CH_3CHO + HO_2 \cdot (17)$$

Acetaldehyde could also be formed from decomposition of the alkoxy radical produced in reaction (11):

$$CH_3CH_2CH_2O \longrightarrow CH_3C \cdot H_2 + HCHO$$
 (18)

The CH₃C·H₂ radical will then follow reactions 13– 17 to eventually lead to acetaldehyde formation. Since the corrected acetaldehyde and propyl formate yields were nearly identical, they appeared to form mainly along the same pathway (reaction 10). The fact that the acetaldehyde yield was the same as the propyl formate yield coupled with the insignificant yield of HCHO suggested that reaction (17) was more likely to occur than reaction (16).

The experimental results in this study support the findings of previous studies on straight-chain ethers. Previous studies with di-ethyl ether [18,19] also determined that decomposition at the C—C bond was more likely than decomposition at the C—O bond. In the di-ethyl ether studies, ethyl formate was the major product and formaldehyde accompanied it with the same yield. The current study indicates that acetaldehyde is produced in the same yield as propyl formate. Unlike di-ethyl ether, the presence of an extra —CH₂— group in the di-*n*-propyl ether chain leads to the production of ethyl radicals rather than methyl radicals from the decomposition of the di-propoxy radical.

One of the two most abundant products, propyl formate, has a tropospheric lifetime of 24.3 days in the atmosphere with respect to reaction with \cdot OH radicals, assuming a tropospheric \cdot OH radical concentration of 2×10^5 molecule cm⁻³ [19]. Acetaldehyde has a lifetime of 3.6 days with respect to •OH attack, and can also photolyze in the troposphere to produce carbon monoxide [9]. Therefore, both propyl formate and acetaldehyde could contribute significantly to photochemical smog formation in the troposphere.

MECHANISM PREDICTIONS

Experimental yields were compared to mechanism predictions developed using the Carter kinetic software [26]. Rate constants were estimated using the SAR [25] method and values from Atkinson [7]. The mechanisms considered attack on all three sets of carbon sites and included isomerization and nitrate reactions. Secondary reactions of the primary products were not included so as to allow for direct comparison of the corrected product yields and the predicted data. Decomposition enthalpies were calculated using NIST values [27]. Decomposition reaction rate values were determined using the following equations [7,28]:

$$k_d = A_d \times e^{-(E_d/RT)} \tag{23}$$

where

$$E_d = a + 0.36 \times \Delta H_d \tag{24}$$

$$A_d = (2.0 \times 10^{14} \, d) \, \mathrm{s}^{-1} \tag{25}$$

d is the path degeneracy for the alkoxy radical decomposition reaction, R is the gas constant (0.00198 kcal $mol^{-1} K^{-1}$), T represents the temperature in Kelvin, and ΔH_d is the decomposition enthalpy in kcal mol⁻¹ [7,28]. The parameter a (kcal mol⁻¹) is dependent on the alkyl leaving-group and has the following values: 11.1 for a primary alkyl radical leaving-group (RC·H2), 9.3 for a secondary alkyl radical leavinggroup ($R_1R_2C \cdot H$), and 7.9 for a tertiary radical leaving-group $(R_1R_2R_3C \cdot)$ [28]. The rate constants for the decomposition pathways were calculated to be 9.04 imes 10^{6} s^{-1} and 697 s⁻¹ for reactions (10) and (11), respectively. Rate constants of 8 \times 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹ and 1.6×10^6 s⁻¹ were used for reactions (9) and (12), as recommended by Atkinson [7,28]. The rate constant used for di-n-propyl ether was 17.2 \times 10^{-12} cm³ molecule⁻¹ s⁻¹ [7]. Nitrate reactions in the form of reaction (26):

$$RO_2 \cdot + NO \longrightarrow RONO_2$$
 (26)

were assigned rate constants according to the method given by Atkinson [7].

Table II provides a comparison between predicted

and observed experimental product yields. Propyl formate and acetaldehyde were predicted as the most abundant products. The mechanism predicted propyl formate's yield within experimental error; however, acetaldehyde's yield was over predicted by 11.7%. The mechanism vastly underpredicted the observed yields of propionaldehyde and propyl propionate.

Product studies of the commercially available primary products revealed no other secondary source of propionaldehyde or propyl propionate. However, the curvatures of the propionaldehyde and propyl propionate plots in Figure 3B support the conclusion of secondary formation of each of these products. It is possible that these products may have been produced from either the OH radical or photolysis reactions of primary nitrate products. As indicated earlier, a product that could not be positively identified because of the lack of a commercially available standard, but had characteristics of a nitrate compound, was observed in the experiments. This nitrate is believed to be 1-propoxy propyl nitrate (formed in reaction 8). Model predictions estimate the 1-propoxy propyl nitrate yield at 0.18, accounting for 18% of the reacted carbon.

The estimated OH radical rate constant of reaction with 1-propoxy propyl nitrate (using the SAR method) was 12.1×10^{-12} cm³ molecule⁻¹ s⁻¹. Hydroxyl radical attack at site IV of 1-propoxy propyl nitrate



formation from the nitrate reaction with OH radicals would then exist:

Pathway 1:

$$CH_{3}CH_{2}CH(ONO_{2})OCH_{2}CH_{2}CH_{3} + \cdot OH \longrightarrow CH_{3}CH_{2}CH(ONO_{2})OC \cdot HCH_{2}CH_{3} + H_{2}O \quad (27)$$

$$CH_{3}CH_{2}CH(ONO_{2})OC \cdot HCH_{2}CH_{3} + O_{2} \longrightarrow CH_{3}CH_{2}CH(ONO_{2})OC(O_{2} \cdot)HCH_{2}CH_{3}$$
(28)

 $\begin{array}{l} CH_{3}CH_{2}CH(ONO_{2})OC(O_{2}\cdot)HCH_{2}CH_{3} + NO \longrightarrow \\ CH_{3}CH_{2}CH(ONO_{2})OC(O\cdot)HCH_{2}CH_{3} + NO_{2} \end{array} (29)$

$$\begin{array}{c} CH_{3}CH_{2}CH(ONO_{2})OC(O \cdot)HCH_{2}CH_{3} \longrightarrow \\ CH_{3}CH_{2}CH(ONO_{2})O \cdot + CH_{3}CH_{2}CHO \quad (30) \end{array}$$

$$CH_{3}CH_{2}CH(ONO_{2})OC(O \cdot)HCH_{2}CH_{3} \longrightarrow CH_{3}CH_{2}CH(ONO_{2})OCHO + CH_{2}CH_{3} \quad (31)$$

Pathway 2:

- $CH_{3}CH_{2}CH(ONO_{2})OCH_{2}CH_{2}CH_{3} + \cdot OH \longrightarrow CH_{3}CH_{2}CH(ONO_{2})OC \cdot HCH_{2}CH_{3} + H_{2}O \quad (27)$
- $CH_{3}CH_{2}CH(ONO_{2})OC \cdot HCH_{2}CH_{3} \longrightarrow CH_{3}CH_{2}C \cdot HONO_{2} + CH_{3}CH_{2}CHO \quad (32)$

Thus, the radical formed as a result of \cdot OH abstraction in reaction (27) could either directly decompose to form propionaldehyde (reaction (32)) or undergo O₂ addition (reaction (28)) followed by NO reduction (reaction (29)) and decomposition to eventually form propionaldehyde (reaction 30). Note that the radical in reaction (32) (CH₃CH₂C·HONO₂) might also decompose to yield propionaldehyde and NO₂.

Hyperchem[®] [29] was used to investigate the formation routes for propionaldehyde from \cdot OH reaction with 1-propoxy propyl nitrate. Unrestricted Hartree Fock (UHF) geometry optimization calculations were performed at the PM3 level for each of the species in reactions (28) and (32). In addition, all species in reactions (30) and (31) were subjected to geometry optimization calculations to investigate the C—O versus C—C decomposition of these two reactions. The heats of formation obtained from the UHF/PM3 calculations were used to determine overall enthalpy changes for the reactions. Although these results are based on semiempirical calculations, they do provide basic insight as to whether or not the overall reactions are energetically favored. The change in enthalpies of

Table II Predicated and Experimental Yields of Detected Products from Di-n-propyl Ether Photooxidation

	Yields	
Compound	Predicted	Experimental (Corrected)
Propyl formate	0.60	0.61 ± 0.044
Acetaldehyde	0.67	0.60 ± 0.057
Propyl propionate	0.0027	0.043 ± 0.015
Propionaldehyde	1×10^{-4}	0.15 ± 0.062
Formaldehyde	$4 imes 10^{-4}$	not detected

reactions (28) and (32) were -16.2 kcal/mol and -32.6 kcal/mol, respectively. Thus, reaction (32) is favored energetically over reaction (28). In addition, if one considers the decomposition pathways of reactions (30) and (31), it is apparent that decomposition at the C—C bond (reaction (31)) is favored over decomposition at the C-O bond (reaction (30)). The enthalpy changes for reactions (30) and (31) are +3.62and -7.99 kcal/mol, respectively. Thus, even if reaction (28) was favored over reaction (32), the formation of propionaldehyde via reaction (30) would most likely be unfavored. However, based on the results, it seems that the most likely fate for alkoxy alkyl nitrate radicals formed from OH abstraction of a hydrogen from the corresponding nitrate is decomposition (reaction (32)) rather than O_2 reaction (reaction (28)).

It is well known that alkyl nitrates in the atmosphere are capable of undergoing photolysis as well as reaction with OH radicals [7]. Thus, it is possible that the alkoxy alkyl nitrate, 1-propoxypropyl nitrate, could photolyze via reaction (33). The subsequent reactions would likely lead to the formation of secondary stable products, including propyl propionate via reaction (34) and two molecules of propionaldehyde via reaction (35):

$$CH_{3}CH_{2}CH(ONO_{2})OCH_{2}CH_{2}CH_{3} + h\nu \longrightarrow$$
$$CH_{3}CH_{2}CH(O \cdot)OCH_{2}CH_{2}CH_{3} + NO_{2} \quad (33)$$

$$CH_{3}CH_{2}CH(O \cdot)OCH_{2}CH_{2}CH_{3} + O_{2} \longrightarrow HO_{2} \cdot + CH_{3}CH_{2}C(O)OCH_{2}CH_{2}CH_{3} \quad (34)$$

$$CH_{3}CH_{2}CH(O \cdot)OCH_{2}CH_{2}CH_{3} \longrightarrow CH_{3}CH_{2}CHO + CH_{3}CH_{2}CHO$$
(35)

Therefore, several pathways may exist for the secondary formation of propionaldehyde and propyl propionate from 1-propoxypropyl nitrate. This result has farreaching implications for nitrates formed from ethers and their potential to act as reservoirs for highly reactive carbonyl-containing compounds. Clearly, additional experimental work on the nitrates formed from the reactions of ethers is warranted.

CONCLUSIONS

The present study has determined that the major pathway of di-*n*-propyl ether photooxidation is via decomposition at the di-propoxy radical C-C bond. This has been confirmed as the major pathway both by analogy with previous studies of di-ethyl ether and from mechanism predictions performed in this study. Propyl formate and acetaldehyde formation proceeded by the C-C decomposition pathway and had the highest yields. Other products, such as propyl propionate and propionaldehyde, were observed in much lower yields. The lower yields of these products indicate that reaction of the dipropoxy radical with O_2 and decomposition at the ether C-O bond, respectively, are minor pathways.

The experimentally determined propionaldehyde and propyl propionate yields observed in this study provide insight into the reactions of nitrates formed from ethers. The results presented suggest secondary formation routes for propionaldehyde and propyl propionate through both the photolysis and •OH-initiated photooxidation of 1-propoxypropyl nitrate. However, additional experimental and/or computational work is needed to fully elucidate the reactions of alkoxy alkyl nitrates.

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