

The Production of Organic Nitrates from Atmospheric Oxidation of Ethers and Glycol Ethers

CYNTIA ESPADA,¹ PAUL B. SHEPSON^{1,2}

¹Departments of Chemistry and Earth and Atmospheric Sciences, Purdue University, West Lafayette, IN 47907

²Purdue Climate Change Research Center, Purdue University, West Lafayette, IN 47907

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ABSTRACT: The production of organic nitrates from OH reaction (in the presence of NO) with methoxy propane, 1-methoxy-2-propanol, ethoxy butane, and 2-butoxyethanol was studied. The measured total organic nitrate yields were 1.8 (± 0.4)%, 0.98 (± 0.2)%, 7.7 (± 2)%, and 9.6 (± 1)%, respectively. The total organic nitrate yield for methoxypropane is 26% of that (7.0%) for *n*-butane. The organic nitrate yield for ethoxy butane is 55% of that (14%) for *n*-hexane. The peroxy radicals produced from OH reaction with the methylene groups α to the ether linkage have an organic nitrate branching ratio (k_{3b}/k_3) value $\sim 50\%$ of those in analogous *n*-alkanes. On the other hand, k_{3b}/k_3 values for peroxy radical functional groups not adjacent to the ether linkage (in γ and δ positions) are on average 1.7 times greater than for the analogous *n*-alkyl peroxy radicals. The organic nitrate formation yield for 1-methoxy-2-propanol is almost half that of methoxy propane, while for 2-butoxyethanol it is 21% greater than that of butoxyethane. Our data lead us to the conclusion that the ether linkage imparts an inductive effect that decreases the value of k_{3b}/k_3 for peroxy radicals adjacent to it, yet has a stabilizing effect, from the additional vibrational modes for those peroxy radicals not adjacent to it, increasing their k_{3b}/k_3 values. The effect of both the —O— and OH groups in these molecules and the importance of their position relative to the peroxy group are discussed in this paper. © 2005 Wiley Periodicals, Inc. *Int J Chem Kinet* 37: 686–699, 2005

INTRODUCTION

Ethers and glycol ethers are used in reformulated gasoline [1] and as industrial solvents and antifreeze in jet

fuels [2]. Since these compounds are emitted into the troposphere, it is important to understand their tropospheric fate, and their contribution to ozone formation. Ozone in the troposphere is a key constituent that determines its oxidizing capability [3], but also affects crops [4] and is a human respiratory irritant [5]. In the troposphere, ethers and glycol ethers will photooxidize by a mechanism similar to that of simple alkanes [6–9], in which OH abstracts an H-atom from the volatile organic compound (VOC) to produce a carbon-centered radical which in turn reacts with O₂ to form an organic

Correspondence to: Paul B. Shepson; e-mail: pshepson@purdue.edu.

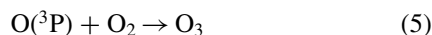
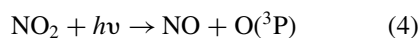
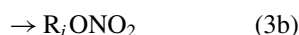
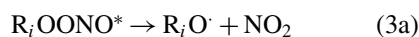
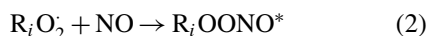
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peroxy radical. The peroxy radicals react with NO to form an unstable peroxy nitrite adduct (reaction (2)), which can dissociate (reaction 3a) or stabilize (reaction (3b)) to form an organic nitrate. This process may also occur [10] in part through formation of a vibrationally excited nitrate that can be stabilized, or dissociate to produce the same products as in reaction (3a).



The OH reaction kinetics and reaction products of some of these ethers and glycol ethers have been studied previously [11,12].

As indicated in reaction (3b), formation of organic nitrates is a termination step, which consumes peroxy radicals and NO_x . This reaction competes with formation of O_3 [13], which occurs through channel (3a) followed by reactions (4) and (5). Therefore, understanding the organic nitrate formation yield of such compounds will shed light on their ozone formation potential.

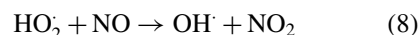
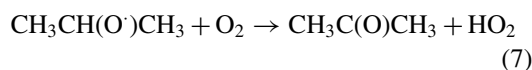
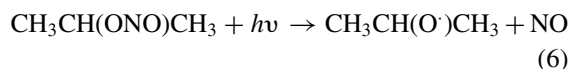
Considerable research has been done concerning organic nitrate formation yields, but mostly for unsubstituted alkanes and alkenes. Arey et al. [14] have reported an updated set of data demonstrating that the organic nitrate yield increases with the size of the precursor molecule, by 30% per $-\text{CH}_2-$ group. O'Brien et al. [15] have determined that yields of organic nitrates from precursor peroxy radicals that contain an OH β - to the peroxy group are significantly smaller than from those with no OH group β - to the peroxy group. It is also known that certain electron-withdrawing substituents (like Br) can affect the value of k_{3b}/k_3 of different peroxy radicals [16].

While it is well known that oxygenated VOCs are among the most important contributors to ozone production on a regional scale basis [17–19], we still do not understand the impact that various oxygen-containing functional groups (such as the ether linkage) have on the stability of the ROONO^* intermediate, and thus the organic nitrate yield. In this paper, we discuss the organic nitrate formation yields for OH reaction with methoxy propane, ethoxy butane, 1-methoxy-2-propanol, and 2-butoxyethanol. We also discuss the determination of the branching ratio, i.e., the fraction of the time that each peroxy nitrite adduct (ROONO^*) will rearrange versus

dissociate (k_{3b}/k_3). These experiments are intended to improve our understanding of the effects of the $-\text{OR}$ and the $-\text{OH}$ functionality in the ROONO^* intermediate. Understanding the effects of these functionalities on the organic nitrate branching ratio will help improve our ability to predict the ozone formation potential of various oxygen-containing VOCs.

EXPERIMENTAL

Experiments were performed using a 5000 L all-Teflon photochemical reaction chamber, at ~ 295 K, and 745 Torr pressure. A mixture of low ppm levels of VOC, isopropyl nitrite (IPN), NO, and low ppb levels of isobutyl nitrate (IBN, the internal standard) was injected into the chamber via a flow of clean dry air. The IPN was used as the source of OH radicals, and the IBN was used as an internal standard, for quantification of organic nitrates. The mixture was irradiated for typical periods of 5 to 12 min. IPN was photolyzed, thus producing OH radicals, as shown below:



The consumption of VOC was measured using gas chromatography with a flame ionization detector, and the production of organic nitrates by gas chromatography with a luminol-based chemiluminescence nitrate detector (LND). The LND consists of a post-column pyrolyzer at 400°C which causes the $\text{O}-\text{NO}_2$ bond in the organic nitrate molecule to cleave, followed by reaction of the NO_2 with luminol (3-aminophthalhydrazide), in a pH 12 aqueous solution [20]. The chemiluminescence is detected by a photomultiplier. As described by Hao et al. [20], the pyrolysis of the organic nitrates is a quantitative process at 400°C . This allows for calibration with any organic nitrate standard, in the absence of adsorptive losses between sample acquisition and detection. Samples were acquired by sampling directly into the cryo-cooled capillary column, through a 20-cm Teflon tubing sampling line, kept at a temperature of 80°C . This procedure minimizes analyte inlet losses [21]. Repetitive injections of the same sample of multifunctional organic nitrates were conducted to ensure reproducible results, as hydroxy nitrates are adsorptive [15,21]. It was found that reproducible results were achieved once the system was conditioned with the analyte species,

as found previously for other multifunctional nitrates. The temperature dependence of the pyrolysis can be used to examine the possibility of detection of compounds other than organic nitrates. At 200°C, the lifetime of the organic nitrates is long compared to their residence time in the pyrolyzer [22], so the signal for the organic nitrate is very small at that temperature. The pyrolyzer temperature was decreased to 200°C to confirm that the observed peaks were organic nitrates. The few species observed at this temperature could be peroxyacyl nitrate compounds, which have very short lifetimes at 200°C [23]. This procedure was performed at least once while running each series of experiments.

MATERIALS AND METHODS

The chemicals used and their corresponding purities were as follows: 1-methoxypropane (96%, TCI America), 1-ethoxy butane (99%, Aldrich), 1-methoxy-2-propanol (98%, Aldrich), 2-butoxyethanol (99%+, Aldrich), isobutyl nitrate (96%, Aldrich), and NO (99%+, Matheson), which were used as purchased, without further purification. IPN was synthesized by dropwise addition of H₂SO₄ to a mixture of NaNO₂ and isopropanol at 0°C, according to Noyes method [24]. 1-Methoxy-2-nitrooxy-propane was synthesized by dropwise addition of H₂SO₄ and 1-methoxy-2-propanol to H₂SO₄, HNO₃, and urea at 0°C, as described by Ranschaert et al. [25], and used as a calibration standard. The purities of IPN and 1-methoxy-2-nitrooxy-propane were assessed using ¹H-NMR.

During these experiments, the VOC concentrations were determined using GC/FID, and the organic nitrate concentrations were determined using GC/LND. The chromatographic conditions were similar to those of Chen et al. [21]. NO and NO₂ concentrations were measured during the experiment using a chemiluminescence NO_x monitor (Thermo Environmental Inc).

The chromatographic conditions were as follows: for the 1-methoxypropane experiments, a 3 m long × 1/8" column packed with Poropack QS, operated isothermally at 110°C, was used to determine the VOC concentration. The organic nitrates were separated using a 30 m long by 0.53 mm i.d. Restek RTX-1701 chromatographic column. For the 1-ethoxy butane experiments, the VOC was determined using a 30 m by 0.53 mm i.d. Restek RTX-1 column, maintained at 85°C. The organic nitrates were separated using a 30 m long by 0.53 mm i.d. Restek RTX-1701 chromatographic column. For both the 1-methoxy-2-propanol and the 2-butoxyethanol experiments, a 30 m by 0.53 mm i.d. Restek RTX-1701 column was used to determine the VOC. For the 1-methoxy-2-propanol case, the column

temperature was 80°C, and in the 2-butoxyethanol case, it was 110°C. The organic nitrates in the 1-methoxy-2-propanol experiment were separated using a 30 m × 0.53 mm i.d. RTX-1 column. In the 2-butoxyethanol case, the very low vapor pressure, polar organic nitrates had relatively long retention times, necessitating the use of a 10 m by 0.53 mm i.d. Restek RTX-1 column.

RESULTS AND DISCUSSION

The objective of these experiments was to determine the organic nitrate yield and the fraction of time a peroxy nitrite intermediate yields an organic nitrate ($k_{3b}/(k_{3a} + k_{3b})$ or "branching ratio") for these model ethers and glycol ethers. Under the conditions of this experiment (in the presence of NO_x), the chemistry in the reaction chamber is such that the VOC will react only with OH and the resulting peroxy radical will react exclusively with NO, forming an unstable adduct [10,26,27], ROONO*. In general, reaction between RO and NO₂ to yield the same organic nitrate as the RO₂ + NO reaction is very slow, relative to the reaction between RO and O₂. Under our experimental conditions, the reaction rate for RO + O₂ is 2–3 orders of magnitude greater than that of RO + NO₂ [27,28]. Thus we expect that formation of RONO₂ via RO + NO₂ is negligible in our experiment. If the latter reaction were important, we would observe upward curvature in the product yield plots as [NO₂] increased during the reaction, and this was never the case (see Fig. 1). Under these conditions, if we can identify the individual isomeric products, we can determine the branching ratio, k_{3b}/k_3 for each specific peroxy radical (R_iO₂·).

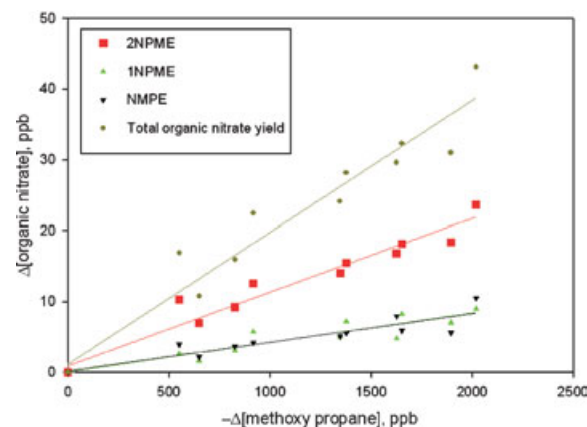


Figure 1 Organic nitrate yield plots for 1-nitrooxypropyl methyl ether, 2-nitrooxypropyl methyl ether, nitrooxymethyl propyl ether and total nitrates.

The rate constant ratio $k_{3b}/(k_{3a} + k_{3b})$ is determined as a result of the fact that under the conditions for these experiments, all organic peroxy radicals react via reaction (2), i.e. $R_1 = R_2 = R_3$. Addition of NO ensures the rate of reaction (2) is dominant over others, such as radical recombination. It also helps suppress the formation of ozone, as well as oxidation of NO_2 to NO_3 . Therefore OH is the only radical that will react with the VOCs. At low pressure ($p \leq 10$ Torr) [8] cleavage of the alkyl radicals can occur. However, at atmospheric pressure the alkyl radicals produced by H-atom abstraction will react exclusively with O_2 , forming an RO_2 radical [8,9]. When all these conditions are met, the rate of consumption of VOC equals the rate of reaction of the peroxy radical adduct, i.e. $-\text{d}[\text{VOC}]/\text{d}t = (k_{3a} + k_{3b})[\text{ROONO}^*]$. Since ROONO^* is very unstable and reactive, it can be assumed that this species is in steady state.

It is of fundamental interest to understand the fraction of each individual ROONO^* intermediate that rearranges to produce a stable nitrate, as a function of molecular structure. To determine this, it is necessary to know the yield of each of the possible peroxy radicals, R_iO_2 . The relative OH abstraction rates (and thus the relative rate of production of the corresponding R_iO_2) can be calculated using the group additivity method of Kwok and Atkinson [29]. Following from the previous assumptions the organic nitrate yield can be determined as shown from Eq. (I).

$$\begin{aligned} (-\text{d}[\text{VOC}]/\text{d}t) \cdot \alpha_i &= \alpha_i \cdot k_1[\text{OH}][\text{VOC}] \\ &= R_{3i} = k_3[\text{R}_i\text{OONO}^*]_{\text{ss}} \end{aligned} \quad (\text{I})$$

Here α_i is the fractional yield of each R_iO_2 isomer formed, and $k_3 = k_{3a} + k_{3b}$.

The rate of production of each organic nitrate is given in Eq. (II):

$$\text{d}[\text{R}_i\text{ONO}_2]/\text{d}t = k_{3b}[\text{R}_i\text{OONO}^*]_{\text{ss}} \quad (\text{II})$$

dividing Eq. (II) by (I), and rearranging, yields

$$\frac{\text{d}[\text{R}_i\text{ONO}_2]/\text{d}t}{-\text{d}[\text{VOC}]/\text{d}t} = \frac{\alpha_i \cdot k_{3b}}{k_3} = \frac{\Delta[\text{R}_i\text{ONO}_2]}{-\Delta[\text{VOC}]} \quad (\text{III})$$

Therefore, from Eq. (III), a plot of $[\text{RONO}_2]$ vs. $-\Delta[\text{VOC}]$ yields a slope corresponding to $\alpha_i \cdot k_{3b}/k_3$ for the specific peroxy radical. Then k_{3b}/k_3 can be determined with use of the calculated values of α_i , using the Kwok and Atkinson method [29]. Based on comparison of calculated α_i values with those obtained experimentally for similar systems, we apply an estimated uncertainty of $\pm 10\%$ to each calculated value

for α_i in the ether experiments. For the 1-methoxy-2-propanol and 2-butoxyethanol cases, experimental data were available [12] for the some of the α_i values used, which improves the uncertainty for those values.

The total organic nitrate yield can be determined from plotting $\Delta[\text{organic nitrate}]$ vs. $-\Delta[\text{VOC}]$. In Fig. 1, we present an example of the organic nitrate yield plot for methoxy propane. Table I shows the results for all compounds studied in the form of chromatographic retention times identified for the products, and their individual and total yields. Tables II and III show the calculated k_{3b}/k_3 values for each peroxy radical as well as comparison using analogous peroxy radicals to calculate the numeric value of the impact of the oxygen atoms in the molecule on the organic nitrate branching ratios. The results for each case are discussed below.

1-Methoxypropane

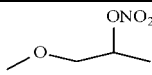
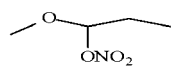
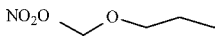
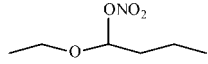
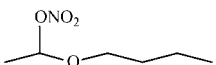
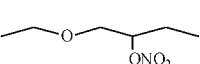
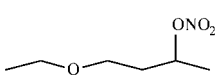
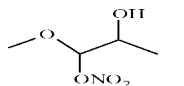
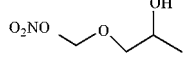
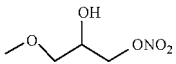
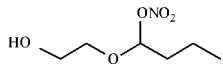
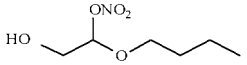
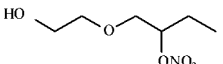
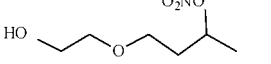
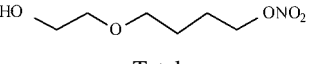
For this reactant, we observed three nitrate products. A standard was available for only one of the possible products, 2-nitrooxypropyl methyl ether. The four expected organic nitrate products for this ether are 3-nitrooxypropyl methyl ether, $\text{CH}_2(\text{ONO}_2)\text{CH}_2\text{CH}_2\text{OCH}_3$ - (3NPME); 2-nitrooxypropyl methyl ether, $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{OCH}_3$ (2NPME); 1-nitrooxypropylmethyl ether, $\text{CH}_3\text{CH}_2\text{CH}(\text{ONO}_2)\text{OCH}_3$ (1NPME); and nitrooxymethyl propyl ether, $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2(\text{ONO}_2)$ (NMPE).

The reaction scheme and structures for these nitrates are shown in Fig. 2. The calculated [29] relative H-atom abstraction rates (α_i) are 0.014, 0.095, 0.80, and 0.094, starting with the methyl end of the propyl side.

The organic nitrate concentrations were corrected for secondary reaction between the organic nitrates and OH, using the Atkinson et al. method [30], and the Kwok and Atkinson [29] method was used for calculation of the OH rate constant for these nitrates. The correction factors were 1.02 for 2NPME, 1.02 for 1NPME, and 1.23 for NMPE (i.e. for those chromatographic peaks assumed to represent those compounds). After this correction, the total concentration of RONO_2 was plotted against the change in concentration of methoxy propane. The total organic nitrate yield from the slope of the plot (Fig. 1) was determined to be $1.8 (\pm 0.4)\%$. This value is 26% of the value 7.0% obtained for the total organic nitrate yield for *n*-butane [14,16] (i.e. the alkane with the same number of carbons). It thus must be that the ether $-\text{O}-$ has a significant negative impact on the RONO_2 formation yield.

The identity of 2NPME, $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{OCH}_3$, was determined by comparison to a standard sample of the individual organic nitrate. According to retention

Table I Results from Individual Organic Nitrate Plots: Slopes and Uncertainties for Each Isomer

Compound	Product	Yield \pm s, (%)	r^2	rt (min)
Methoxy propane		1.01 \pm 0.2	0.96	18.1
		0.44 \pm 0.1	0.90	17.9
		0.31 \pm 0.08	0.87	21.8
	Total	1.8 \pm 0.4	0.92	–
	Ethoxy butane		4.8 \pm 0.9	0.96
Ethoxy butane		2.4 \pm 0.6	0.96	21.5
		0.33 \pm 0.08	0.72	20.5
		0.28 \pm 0.07	0.87	21.0
	Total	7.7 \pm 2	0.81	–
	1-Methoxy-2-propanol		0.58 \pm 0.2	0.88
1-Methoxy-2-propanol		0.34 \pm 0.09	0.93	24.5
		0.09 \pm 0.02	0.92	27.1
	Total	0.98 \pm 0.2	0.91	–
	2-Butoxyethanol		3.4 \pm 0.7	0.89
2-Butoxyethanol		2.7 \pm 0.6	0.75	29.8
		2.4 \pm 0.5	0.75	31.2
		0.62 \pm 0.1	0.62	31.1
		0.49 \pm 0.1	0.63	30.1
	Total	9.6 \pm 1	0.82	–

time match, this is the main product, with a formation yield of 1.0 (\pm 0.2)%, after correction for secondary reaction with OH. The chromatographic peak corresponding to the second greatest yield ($0.44 \pm 0.1\%$) has a retention time very close to the 2NPME peak. We suspect this peak corresponds to either 1NPME

or 3NPME, which we expect to have the most similar retention times. The relative OH abstraction rate (α) for production of the precursor to 1NPME, i.e., $\text{CH}_3\text{CH}_2\text{CH}(\text{OO}\cdot)\text{OCH}_3$, is over 56 times greater than that for $\text{CH}_2(\text{OO}\cdot)\text{CH}_2\text{CH}_2\text{OCH}_3$, and 8 times greater than that for $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{OO}\cdot$, leading us to

Table II Effect of α Ether Linkage on the k_{3b}/k_3 Values for Each RO_2

Radical	Carbon Type	k_{3b}/k_3 Value	Analogous Compound	k_{3b}/k_3 Analogous	α Ether Linkage Effect
	2°	0.006 ± 0.003		0.07 [16]	0.079
	2°	0.06 ± 0.03		0.15 [14]	0.42
	2°	0.10 ± 0.06		0.15 [14]	0.68
	2°	0.010 ± 0.006		0.034 [15]	0.29
	2°	0.05 ± 0.01		0.055 [15]	0.85
	1°	0.033 ± 0.02		0.077 [16]	0.43
					Average = 0.45 ± 0.27

believe that this peak corresponds to 1NPME. The chromatographic peak corresponding to the smallest yield was the last peak to elute, more than a minute apart from the other two nitrates. This retention time coupled with the fact that the relative abstraction rate leading to the peroxy radical that will form NMPE, i.e. $CH_3CH_2CH_2OCH_2OO\cdot$, is 6.8 times greater than that of the 3NPME precursor, $CH_2(OO\cdot)CH_2CH_2OCH_3$, leads us to believe that the smallest detected peak corresponds to NMPE. We believe that 3NPME would be formed in such small yield that its concentration would have been below the limit of detection of our method.

From a plot of $[2NPME]$ vs. $-\Delta[MP]$, we obtain a value for the branching ratio (k_{3b}/k_3) for the $CH_3CH(OO\cdot)CH_2OCH_3$ radical of $0.0101 (\pm 0.002)/$

$0.095 = 0.11 \pm 0.06$. This value is 57% higher than our measured value of 0.07 for $CH_3CH(OO\cdot)CH_2CH_3$ radicals [16]. We believe this represents an oxygen substituent stabilization effect, i.e. the additional vibrational modes from the $-O-$ group will help the $ROONO^*$ adduct dissipate the excess energy related to formation of the new bond. It has been discussed in Carter and Atkinson [26] and Arey et al. [14] that the organic nitrate branching ratios increase linearly with the number of $-CH_2-$ groups in alkyl peroxy radicals, with a slope of 1.3 (i.e., a 30% increase per $-CH_2-$ group in the molecule, as shown by the open squares in Fig. 6 discussed below). To further support this effect, we find that the branching ratio for $CH_2(Br)CH_2CH_2(OO\cdot)$ radicals is 1.45 times greater than that for nonsubstituted $CH_3CH_2CH_2OO\cdot$ radicals [16]. In the case of the

Table III Effect of Oxygen Substituents^a on the k_{3b}/k_3 Values for Each RO_2

Radical	Carbon Type	k_{3b}/k_3 Value	Analogous Compound	k_{3b}/k_3 Analogous	Substituent Effect
	2°	0.11 ± 0.06		0.07 [16]	1.6
	1°	0.069 ± 0.03		0.033 ^b	2.1
	2°	0.19 ± 0.06		0.15 [14]	1.1*
	2°	0.57 ± 0.2		0.15 [14]	1.9*
	1°	0.61 ± 0.03		0.15 [14]	2.0*
	2°	0.16 ± 0.04		0.11 ^b	1.4
					Average = 1.7 (±0.4)

The substituent effect values for compounds with two oxygen atoms (mark with * in this table) were calculated by determining the square root of $(k_{3b}/k_{3ether})/(k_{3b}/k_{3analogous})$.

Others were determined by $(k_{3b}/k_{3ether})/(k_{3b}/k_{3analogous})$.

^a For those radicals for which the substituent is not α - or β - to $-OO\cdot$ group.

^b Determined in this work. See text for details.

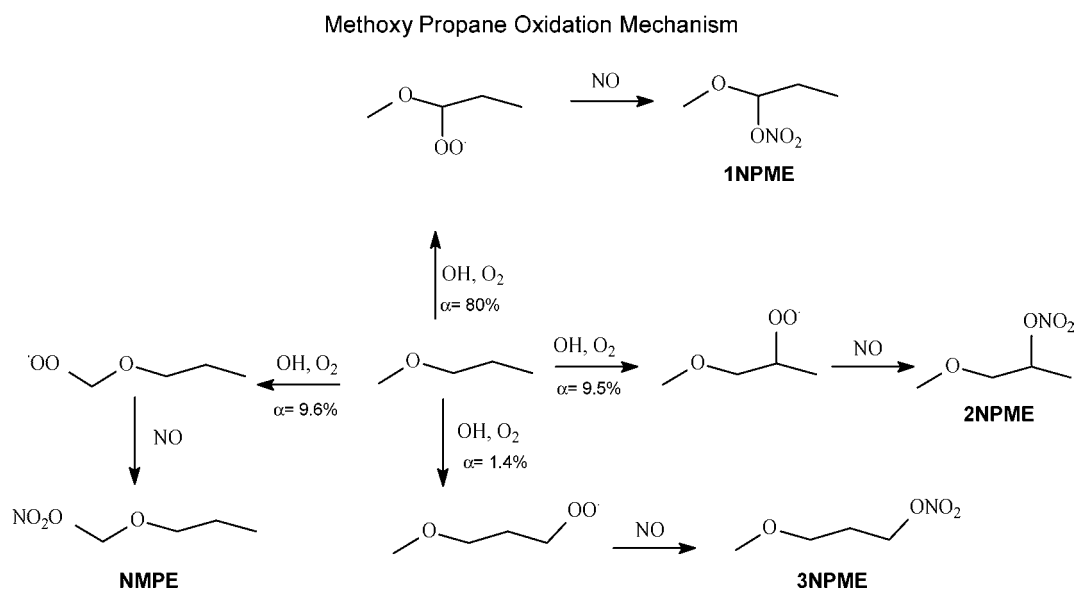


Figure 2 Methoxy propane photooxidation mechanism relative abstraction rates and possible organic nitrate products.

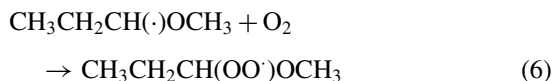
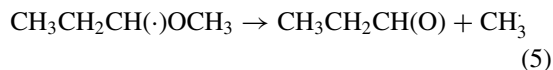
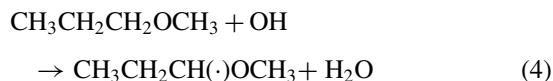
ether, we calculate that the additional O atom increases the branching ratio by a factor of 1.57.

The branching ratio for the peroxy radical precursor of 1NPME ($\text{CH}_3\text{CH}_2\text{CH}(\text{OO}\cdot)\text{OCH}_3$) is $0.0044 (\pm 0.001)/0.80 = 0.006 \pm 0.003$. This value is ~ 12 times smaller than our measured value for $\text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}_2\text{CH}_3$ radicals [16], and implies a large inductive effect from the presence of an α ether linkage. Presumably, the inductive effect results in a weakening of the O—O bond in the peroxy nitrite intermediate. We can compare this result to the value for the case of a β -Br, which also weakens the O—O bond because of an inductive effect [16]. The value for k_{3b}/k_3 for 1-bromo-2-peroxy-propyl radicals is 0.022, or a destabilization effect of 0.56 [16]. There are no other published data on the effects of an α substituent on the organic nitrate yield, so we cannot establish a significant comparison.

It is most likely that the third peak corresponds to NMPE with a yield of $0.31 (\pm 0.08)\%$ and the branching ratio, k_{3b}/k_3 , for the precursor radical $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{OO}\cdot$ is $0.0031 (\pm 0.0008)/0.094 = 0.033 \pm 0.02$. This value is 43% of that for the primary butyl peroxy radicals determined by this group [16], and is 5.3 times greater than that calculated above for $\text{CH}_3\text{CH}_2\text{CH}(\text{OO}\cdot)\text{OCH}_3$ radicals. The α -oxygen inductive effect is present but not nearly as great as in the 1NPME case, indicating that the magnitude of the inductive effect is sensitive to the nature of the alkyl substituents.

It is interesting that the formation rate of the peroxy radical precursor for 1NPME $\text{CH}_3\text{CH}_2\text{CH}(\text{OO}\cdot)\text{OCH}_3$ is more than eight times greater than for the one that yields the main observed nitrate, 2NPME

($\text{CH}_3\text{CH}(\text{OO}\cdot)\text{CH}_2\text{OCH}_3$), which has a yield more than double that of 1NPME. We considered that the low formation yields for 1NPME and NMPE could be due to bond cleavage in the carbon-centered radical as shown in the following reactions:



However, according to Sehested et al. [8] and Maricq et al. [9], reaction (5) competes with reaction (6) only at low pressure (10 Torr and lower). At atmospheric pressure, addition of oxygen (reaction (6)) is the dominant path. This leads us to believe that there is an inductive effect that weakens the O—ONO bond when the ether linkage is on the α carbon, but an oxygen atom substituent effect that increases the k_{3b}/k_3 (by stabilizing the peroxy nitrite through the additional vibrational modes) when the ether linkage group is not on the α carbon.

Ethoxy Butane

We observed four organic nitrate product peaks. The total organic nitrate yield for this compound was determined to be $7.7 (\pm 2)\%$, after correction for secondary reaction with OH. This is 55% of the

14.1% yield obtained for *n*-hexane [14] (with the same number of carbon atoms). Again, we think this decrease is caused by the negative impact the ether linkage has on the peroxyxynitrite intermediates for the isomers involving an α nitrooxy group. The calculated relative rates of H-atom abstraction by OH, starting from the methyl end of the butyl side are 0.008, 0.056, 0.069, 0.473, 0.385, and 0.008. In that order, the six expected organic nitrates are 4-nitrooxybutyl ethyl ether (4NBEE), $\text{CH}_2(\text{ONO}_2)\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$; 3-nitrooxybutyl ethyl ether (3NBEE), $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$; 2-nitrooxybutyl ethyl ether (2NBEE), $\text{CH}_3\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{OCH}_2\text{CH}_3$; 1-nitrooxybutyl ethyl ether (1NBEE), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{ONO}_2)\text{OCH}_2\text{CH}_3$; 1-nitrooxyethyl butyl ether (1NEBE), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}(\text{ONO}_2)\text{CH}_3$; and 2-nitrooxyethyl butyl ether (2NEBE), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2(\text{ONO}_2)$. The mechanism and structures of these six nitrates are shown in Fig. 3. Four of the six possible products were observed. There are no standards that we can use to identify each peak, but we can assign the peaks as a function of their retention times and their calculated yield. We can apply what we learned in the methoxy propane case about the effect of the ether linkage on the branching ratio to determine k_{3b}/k_3 for each peroxy radical in ethoxy

butane. To estimate the expected organic nitrate yields, we start by assuming a value for k_{3b}/k_3 of 0.15 for the secondary hexylperoxy radical [14], and multiply it by an estimated average correction factor ϕ of 0.50 for the destabilization effect of having an alpha ether oxygen, or by 1.57 for the stabilization effect for peroxy radicals with β , γ , or δ ether linkages, assuming there is no significant difference in the k_{3b}/k_3 for primary vs. secondary peroxy radicals [16]. We can then estimate the individual organic nitrate yields as $\alpha \cdot \phi \cdot 0.15$, where α is the calculated fractional H abstraction rate, and ϕ is the appropriate correction factor (i.e. either 0.50 or 1.57). This approach yields $(0.008)(.15)(1.57) = 0.19\%$ for 4NBEE; $(0.056)(.15)(1.57) = 1.32\%$ for 3NBEE; $(0.069)(.15)(1.57) = 1.62\%$ for 2NBEE; $(0.473)(.15)(0.5) = 3.55\%$ for 1NBEE; $(0.385)(.15)(0.5) = 2.89\%$ for 1NEBE; and $(0.008)(.15)(1.57) = 0.19\%$, for 2NEBE. The calculated sum of the yields is 9.8%. This value is not significantly different from our determined yield of $7.7(\pm 2)\%$. We assume these results to be representative of the relative importance of the organic nitrates, and thus useful in chromatographic peak assignment. We expect that the concentrations of 4NBEE and 2NEBE would be much too low to be detected by our system, and thus it is sensible that only four nitrates were observed.

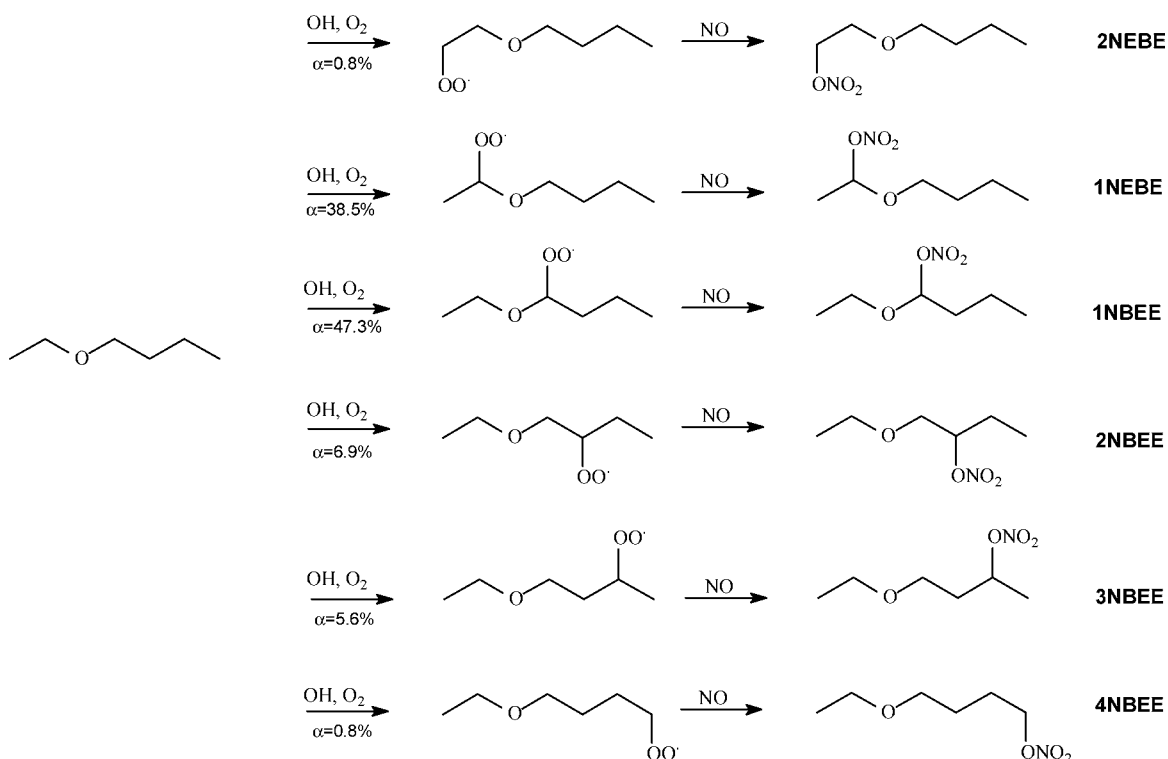


Figure 3 Ethoxy butane photooxidation mechanism, relative abstraction rates, and possible organic nitrate products.

This calculation leads us to believe the product in largest yield should be 1NBEE. The observed yield for this isomer is $4.8(\pm 0.9)\%$, after correction for secondary OH reaction [30] ($F = 1.09$), and the calculated branching ratio $k_{3b}/k_3 = 0.048/0.473 = 0.10 \pm 0.06$ for the $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OO}^\cdot)\text{OCH}_2\text{CH}_3$ radicals. This can be compared to that for 2-hexyl peroxy radicals (0.15), indicating again a destabilizing effect of an ether linkage α to the peroxy nitrite intermediate of 0.67.

The second most abundant organic nitrate should be 1NEBE. This peak assignment would also make sense, since the retention times of this species and that identified as 1NBEE are very similar. The yield of 1NEBE is $2.4(\pm 0.6)\%$, after correction for secondary OH reaction ($F = 1.09$), and the branching ratio, $k_{3b}/k_3 = 0.024(\pm 0.006)/0.385(\pm 0.04) = 0.06 \pm 0.03$ for the $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}(\text{OO}^\cdot)\text{CH}_3$ radicals. The value 0.06 is only 41% of that for secondary peroxy hexyl radicals, again indicating a significant destabilizing effect from an ether linkage in the α position. This result is consistent with what we learned in the methoxy propane case.

The next most abundant organic nitrate product should be 2NBEE, according to our previous calculation. The yield for 2NBEE is $0.33(\pm 0.08)\%$, after correction for secondary OH reaction ($F = 1.09$) and the calculated branching ratio $k_{3b}/k_3 = 0.0033(\pm 0.0008)/0.069(\pm 0.007) = 0.05 \pm 0.03$ for the $\text{CH}_3\text{CH}_2\text{CH}(\text{OO}^\cdot)\text{CH}_2\text{OCH}_2\text{CH}_3$ radicals. This value is only 32% of that for secondary hexyl peroxy radicals [14]. This number is unexpectedly low, as our best estimate would be $0.15 \cdot 1.57 = 0.24$; inductive effects should not affect the peroxy nitrites in β or γ positions.

A similar result was obtained for 3NBEE, the organic nitrate with the smallest observed yield. If our identification is correct, its corrected yield is $0.28(\pm 0.07)\%$ ($F = 1.17$) and the calculated branching ratio, $k_{3b}/k_3 = 0.0028(\pm 0.0007)/0.056(\pm 0.006) = 0.05 \pm 0.03$ for the $\text{CH}_3\text{CH}(\text{OO}^\cdot)\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ radicals. Again, we expected this value to be greater than that for secondary peroxy radicals in *n*-hexane, since the oxygen would increase the number of vibrational degrees of freedom in the peroxy nitrite intermediate. This value is only 33% of that for secondary peroxy radicals in *n*-hexane [14]. As the only other sensible alternative possibility, we can consider that the formation yield order is 2NBEE, 3NBEE, 1NBEE, and 1NEBE, in order of decreasing importance. Using this order of relative yields, the calculated branching ratio for $\text{CH}_3\text{CH}_2\text{CH}(\text{OO}^\cdot)\text{CH}_2\text{OCH}_2\text{CH}_3$ radicals would be 0.7 ± 0.3 . This is unrealistically high. The largest reported branching ratio for any peroxy radical is 0.39 for 1-peroxy octyl radicals [31]. The

branching ratio for $\text{CH}_3\text{CH}(\text{OO}^\cdot)\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ radicals would be 0.4 ± 0.2 , and the stabilization factor for the ether $-\text{O}-$ would be 2.9, again much higher than expected. The branching ratio for $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OO}^\cdot)\text{OCH}_2\text{CH}_3$ radicals would be 0.009 ± 0.003 , and the numeric value for the effect of having an ether linkage next to the peroxy group would be 0.06, which is an order of magnitude lower than that obtained for analogous peroxy radicals.

These values are harder to reconcile than the previous, and the value 0.44 as the destabilizing effect of having an alpha ether linkage is the most consistent result, according to what we have learned in the methyl propyl ether case. Therefore, we believe that our original proposed identification order produces the most self-consistent set of results and thus we assume is correct, and the possible errors in these branching ratios are not due to errors in peak identification.

1-Methoxy-2-propanol

Given the information about methyl propyl ether, 1-methoxy-2-propanol allows us to investigate the impact of the OH group on the RONO_2 yields. For this species, we expect three organic nitrates to be produced, specifically: 1-methoxy-3-nitrooxy-2-propanol (1M3N2P), $\text{CH}_2(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}_2\text{OCH}_3$; 1-methoxy-1-nitrooxy-2-propanol (1M1N2P), $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{OCH}_3$; and 1-nitrooxy-methoxy-2-propanol (1NM2P), $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OCH}_2\text{ONO}_2$. The mechanism and structures of the product nitrates are shown in Fig. 4. H atom abstraction from the $-\text{CH}_2(\text{OH})-$ group will lead to formation of methoxy acetone [6,12]. We have identified three chromatographic peaks as being organic nitrates. The total organic nitrate yield is $0.98(\pm 0.2)\%$, after correction for secondary reaction between the organic nitrates and OH. The magnitude of the correction factors was 1.05 for 1M3N2P, 1.01 for 1M1N2P, and 1.07 for 1NM2P. This total yield is consistent with the Tuazon et al. upper limit of 2% for organic nitrates [12], and is only 14% of that for *n*-butane [14,16], and half of that reported above for methoxy propane. Thus it is clear that the $-\text{OH}$ substituent has had a significant effect on the organic nitrate yield, as observed previously [15].

Using the method of Kwok and Atkinson [29], Tuazon et al. [12] calculated that the relative hydrogen atom abstraction frequencies via OH reaction with 1-methoxy-2-propanol are 1%, 43%, 50%, and 6%, starting from the methyl end of the propyl group. However, according to their experimental data, $59(\pm 5)\%$ of the H abstractions occur at carbon #3, counting from the propyl group. From Kwok and Atkinson [29], we know that abstraction from the methoxy group will occur

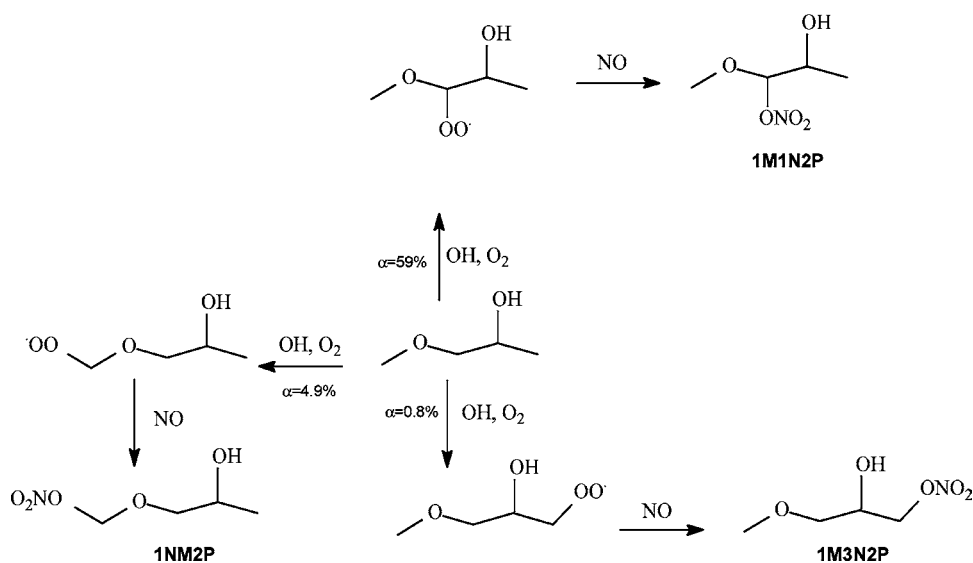


Figure 4 1-Methoxy-2-propanol photooxidation mechanism, relative abstraction rates and possible organic nitrate products.

~six times faster than from the methyl group on the propanol side. Therefore, using the Tuazon et al. experimental values [12] and calculating accordingly for the two methylene groups, we obtain the following relative H abstraction rates for 1-methoxy-2-propanol: $0.8(\pm 0.6)\%$, $35(\pm 4)\%$, $59(\pm 5)\%$, and $4.9(\pm 2)\%$, starting from the methyl end in the propyl group. The uncertainties in the α values calculated on the basis of the Tuazon et al. study are so large for the methyl groups that these numbers are not useful in any quantitative kinetic sense. Therefore, we cannot calculate k_{3b}/k_3 values for the precursors to 1M3N2P or 1NM2P.

Although we do not have standards for these nitrates, we can make reasonable assumptions to identify them according to what we have learned from the ethers. We assume a value of 0.07 for the branching ratio for butyl peroxy radicals from butane [14,16], 0.5 for the destabilization effect of having an alpha ether (the average of the alpha ether linkage effect on $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2(\text{OO}\cdot)$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OO}\cdot)\text{OCH}_2\text{CH}_3$, and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}(\text{OO}\cdot)\text{CH}_3$ as shown in Table II), a factor of 0.5 for the destabilization effect of having an OH group β to the peroxy nitrite group [15]; and a stabilization factor of 1.57 for the OH group when not β to the OONO group, as determined for $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OCH}_2(\text{OO}\cdot)$. We can estimate the formation yield for each organic nitrate as $\alpha \cdot k_{3b}/k_3 \cdot \phi$, where α is the relative hydrogen abstraction frequency, k_{3b}/k_3 is the branching ratio for the analogous alkylperoxy radical, and ϕ is the corresponding correction factor. The estimated yields are $(0.008)(0.07)(1.57)(0.5) = 0.044\%$ for 1M3N2P, $(0.59)(0.07)(0.5)(.5) = 1.05\%$ for 1M1N2P,

and $(0.049)(0.07)(0.5)(1.57) = 0.27\%$ for 1NM2P. This leads to a predicted total yield of 1.36%, or only 39% more than the observed value.

H abstraction from the $-\text{CH}_2(\text{OH})-$ group will not lead to an organic nitrate, but to methoxy acetone. Therefore, the main organic nitrate should be $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{ONO}_2)\text{OCH}_3$, 1M1N2P. If our identification is correct, its yield is $0.58(\pm 0.2)\%$. From this we can calculate the branching ratio making use of our estimate for α , i.e. $k_{3b}/k_3 = 0.0058/0.59 = 0.010 \pm 0.006$ for $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{OCH}_3$ radicals. This value is only 14% of the value for *n*-peroxy butyl radicals [16] (i.e. with the same number of carbon atoms). This result is consistent with our expectations, since the peroxy radical precursor to 1M1N2P has both an α -ether oxygen and a β -OH group, both of which decrease the yield. Using the value of 0.07 for k_{3b}/k_3 for secondary peroxy radicals for *n*-butane, 0.5 for the negative effect of having an OH β to the peroxy nitrite group, and 0.5 for the average negative effect of having an ether linkage next to the peroxy group (average of ether values), we obtain a calculated $k_{3b}/k_3 = 0.018$, which is close to that obtained experimentally (i.e. 0.010 ± 0.006). However, we obtained a value of $k_{3b}/k_3 = 0.0055$ for $\text{CH}_3\text{CH}_2\text{CH}(\text{OO}\cdot)\text{OCH}_3$ radicals. These two results are inconsistent as we expect the k_{3b}/k_3 value for radicals such as $\text{CH}_3\text{CH}(\text{OH})\text{CH}(\text{OO}\cdot)\text{OCH}_3$ to be negatively affected by the β -OH group, and therefore to have a smaller branching ratio, k_{3b}/k_3 , than for the $\text{CH}_3\text{CH}_2\text{CH}(\text{OO}\cdot)\text{OCH}_3$ case. This could indicate that the k_{3b}/k_3 value for the latter radical (precursor to 1NPME) might not be correct.

We can also compare the value for $\text{CH}_3\text{CH}(\text{OH})\text{-CH}(\text{OO}\cdot)\text{OCH}_3$ radicals to that for $\text{CH}_3\text{CH}(\text{OH})\text{C}(\text{OO}\cdot)\text{CH}_3$, i.e. 2-hydroxy-3-peroxy butyl radicals (0.034) [15]. Our value for k_{3b}/k_3 for $\text{CH}_3\text{CH}(\text{OH})\text{-CH}(\text{OO}\cdot)\text{OCH}_3$ is 29% of that for 2-hydroxy-3-peroxy butyl radicals, which corresponds to the correction for an ether linkage next to the peroxy nitrite intermediate. This value of 0.29 is about half what we obtained for the ethers, but still consistent with the result that branching ratios are negatively affected by peroxy nitrates with alpha ether linkages.

We expect the second largest peak to be 1NM2P, $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OCH}_2\text{ONO}_2$, and its yield is 0.34 (± 0.09)%. We then calculate the k_{3b}/k_3 value for $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{OCH}_2\text{OO}\cdot$ radicals as $0.0034 (\pm 0.09)/0.049 (\pm 0.02) = 0.069 (\pm 0.03)$. We can compare this value to the value $k_{3b}/k_3 = 0.033 (\pm 0.02)$ for $\text{CH}_3\text{CH}_2\text{CH}_2\text{OCH}_2\text{OO}\cdot$ radicals determined above. As we can see, this results in an enhancement factor of 2.1 for the presence of an $-\text{OH}$ group that is other than β - to the peroxy group. Although this is relatively large, compared to the value 1.57 obtained above for an $-\text{O}-$ group, it is a consistent effect.

We expect $\text{CH}_2(\text{ONO}_2)\text{CH}(\text{OH})\text{CH}_2\text{OCH}_3$ (1M3N2P) to have the smallest organic nitrate yield. If this identification is correct, its yield is 0.09 (± 0.02)%. For this species, the uncertainty of the value for the relative H abstraction frequency (0.8%) is too large for it to be kinetically useful, i.e. with any reliability.

2-Butoxyethanol

2-Butoxyethanol, in comparison to ethyl butyl ether, presents another opportunity to investigate the impact of oxygen substituents on the organic nitrate branching ratios, in part through comparison to the results for ethyl butyl ether. The expected products are 4-nitrooxybutoxy-2-ethanol (4NB2E), $\text{CH}_2(\text{ONO}_2)\text{CH}_2\text{CH}_2\text{-CH}_2\text{OCH}_2\text{CH}_2(\text{OH})$; 3-nitrooxybutoxy-2-ethanol (3NB2E), $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2(\text{OH})$; 2-nitrooxybutoxy-2-ethanol (2NB2E), $\text{CH}_3\text{CH}_2\text{CH}(\text{ONO}_2)\text{CH}_2\text{OCH}_2\text{CH}_2(\text{OH})$; 1-nitrooxybutoxy-2-ethanol (1NB2E), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{ONO}_2)\text{OCH}_2\text{-CH}_2(\text{OH})$; and 1-butoxy-1-nitrooxy-2-ethanol (B1N2E), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}(\text{ONO}_2)\text{CH}_2(\text{OH})$.

The mechanism and structure of the nitrates are presented in Fig. 5. When OH abstracts an H atom from the $-\text{CH}_2\text{OH}$ group, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CHO}$ is produced. Starting from the butyl end, the calculated fractional H-atom abstraction rates are 1%, 4%, 5%, 37%, 37%, and 15%, using the Kwok and Atkinson method [29]. However, based on the product data, Tuazon et al. [12] estimate that 21 (± 2)% occurs from carbon #4, starting from the methyl end on the butoxy side, forming the $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OO}\cdot)\text{OCH}_2\text{CH}_2(\text{OH})$ radical, and 57 (± 5)% via carbon #5, counting similarly, forming the $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}(\text{OO}\cdot)\text{CH}_2(\text{OH})$ radical. Using the experimental values determined by Tuazon et al. [12], and scaling the difference, i.e. 22%, given the

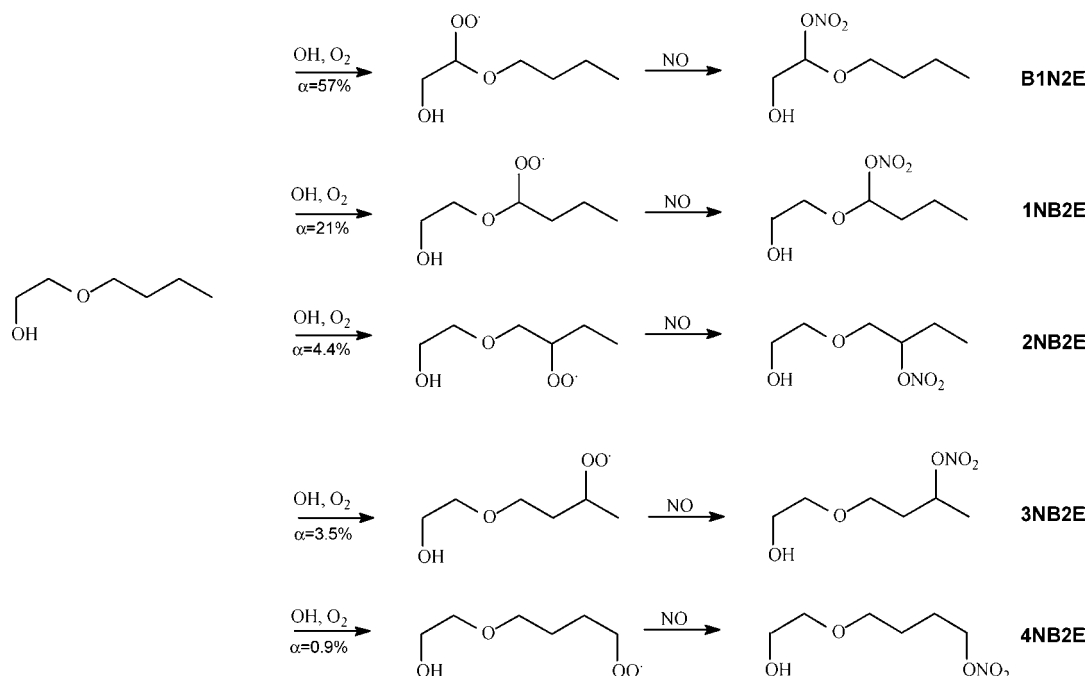


Figure 5 2-Butoxy ethanol photooxidation mechanism, relative abstraction rates, and possible organic nitrate products.

relative abstraction rates from the Kwok and Atkinson method, our estimates of the α values for each carbon atom are 0.9%, 3.5%, 4.4%, 21%, 57%, and 13%, starting from the methyl group on the butyl end.

We observed five organic nitrate peaks. The observed overall organic nitrate yield is $9.6 (\pm 1)\%$, after correction for secondary reaction with OH. The correction factors were 1.3 for 4-nitrooxybutoxy 2-ethanol, 1.06 for 3-nitrooxybutoxy-2-ethanol, 1.08 for 2-nitrooxybutoxy-2-ethanol, 1.01 for 1-nitrooxybutoxy-2-ethanol, and 1.2 for 1-butoxy-1-nitrooxy-2-ethanol. This total organic nitrate yield is in very good agreement with the value of $10 \pm 3\%$, reported by Tuazon et al. [12].

As previously discussed, we will use the branching ratio value for *n*-hexane and the corresponding substituent factors to estimate the relative yield of each organic nitrate, and then use those estimates to support peak assignments. We will calculate the expected yield using a branching ratio of 0.15 for hexyl peroxy radicals [14], 0.5 for the destabilizing effect from an alpha ether linkage, 0.5 for the destabilization effect of an OH group β to the peroxy nitrite group [15], and 1.57 for the stabilization effect of an oxygen atom ($-\text{O}-$ or OH) that is further than β - to the $\text{O}-\text{ONO}$ group. The estimated organic nitrate yields are $(0.009)(0.15)(1.57)(1.57) = 0.33\%$ for 4NB2E, $(0.035)(0.15)(1.57)(1.57) = 1.29\%$ for 3NB2E, $(0.042)(0.15)(1.57)(1.57) = 1.63\%$ for 2NB2E, $(0.21)(0.15)(0.5)(1.57) = 2.52\%$ for 1NB2E, and $(0.57)(0.15)(0.5)(0.5) = 2.18\%$ for B1N2E. The calculated total organic nitrate yield is 7.9%, which is 82% of that determined experimentally.

From this calculation, we expect 1NB2E to be the organic nitrate produced in the greatest yield. Assuming our identification is correct, its yield is $3.4 (\pm 0.7)\%$ and the calculated $k_{3b}/k_3 = 0.034 (\pm 0.007)/0.21 = 0.16 \pm 0.04$ for the $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OO}^\cdot)\text{OCH}_2\text{CH}_2(\text{OH})$ radical. This value is very similar to that for secondary carbons in *n*-hexane [14]. As discussed above, we obtained a value $k_{3b}/k_3 = 0.11$ for $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OO}^\cdot)\text{OCH}_2\text{CH}_3$ radicals. Thus from this pair, we obtain a stabilization factor for the OH group not in an alpha position of $0.16/0.11 = 1.45$. This value is in good agreement with previous stabilization factors for peroxy nitrite intermediates β and γ to ether linkages, as well as Br-atom stabilization [16].

We assume that the second most abundant nitrate should be B1N2E. The measured yield for this nitrate is $2.7 (\pm 0.6)\%$ and we calculate $k_{3b}/k_3 = 0.027(\pm 0.006)/0.57 = 0.05 \pm 0.01$ for $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}(\text{OO}^\cdot)\text{CH}_2(\text{OH})$ radicals. The predicted k_{3b}/k_3 in this case is $(0.15)(0.5)(0.5) = 0.038$. The

value 0.047 is 26% of that for 2-hexyl peroxy radicals [14], and 67% of that for the corresponding peroxy radical in ethyl butyl ether. For this case, the calculated value for β -OH destabilization is 0.67. If we compare the k_{3b}/k_3 value for $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}(\text{OO}^\cdot)\text{CH}_2\text{OH}$ radicals to that for $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{OO}^\cdot)\text{CH}_2\text{OH}$ radicals (0.055) [15], we calculate a value for the effect of having an ether linkage in the α position of $0.047/0.055 = 0.85$. This is a smaller effect than obtained with the simple ethers, but still consistent in direction.

We expect the third largest nitrate to be 2NB2E. The measured yield is $2.4 (\pm 0.5)\%$ and we calculate $k_{3b}/k_3 = 0.024(\pm 0.005)/0.044 = 0.54 \pm 0.2$ for $\text{CH}_3\text{CH}_2\text{CH}_2(\text{OO}^\cdot)\text{CH}_2\text{OCH}_2\text{CH}_2(\text{OH})$ radicals. This value is ~ 3.6 times that for secondary peroxy radicals in *n*-hexane [14], and 12 times that for the corresponding peroxy radical in the ethyl butyl ether case, $\text{CH}_3\text{CH}_2\text{CH}(\text{OO}^\cdot)\text{CH}_2\text{OCH}_2\text{CH}_3$. This value is significantly greater than the branching ratio for any peroxy radical reported in the literature, and it seems improbable. If we use $\alpha = 0.05$, as calculated directly via the Kwok and Atkinson method, then the calculated $k_{3b}/k_3 = 0.48$. If we accept the value 0.54, calculation of the average stabilization effect (x) for the two oxygen atoms leads to $0.54 = 0.15(x^2)$, where 0.15 is the k_{3b}/k_3 for secondary peroxy hexyl radicals and x is then 1.90, which is in fact not inconsistent with the O-group substituent effects obtained to this point (and as summarized in Table III).

The next most abundant nitrate is assumed to be 3NB2E. Its yield is $0.62 (\pm 0.1)\%$ and we calculate $k_{3b}/k_3 = 0.0062(\pm 0.001)/0.035 = 0.18 \pm 0.06$ for $\text{CH}_3\text{CH}(\text{OO}^\cdot)\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2(\text{OH})$ radicals. This value is 1.2 times that for secondary peroxy hexyl radicals [14], likely due to the stabilization by the two additional heavy atoms. In this case, if we determine the numeric value for the O atom stabilization, we obtain an average of $0.18 = (0.15)(x^2)$, and $x = 1.09$. It is important to note that the value 0.18 is nearly four times that obtained for $\text{CH}_3\text{CH}(\text{OO}^\cdot)\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ radicals. Since the only difference is the OH group, we would have expected a much smaller difference, leading us to believe that the branching ratio value, $k_{3b}/k_3 = 0.050$, for $\text{CH}_3\text{CH}(\text{OO}^\cdot)\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$ radicals (the previously discussed peroxy radical) is not correct.

We expect the smallest observed peak to be 4NB2E. If this identification is correct, the yield for this nitrate is $0.49 (\pm 0.1)\%$ and $k_{3b}/k_3 = 0.0049/0.009 = 0.54(\pm 0.3)$ for $\text{CH}_2(\text{OO}^\cdot)\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2(\text{OH})$ radicals. This is significantly larger than the expected value, $(0.15)(1.57)(1.57) = 0.37$. We do not have information about the analogous unsubstituted peroxy

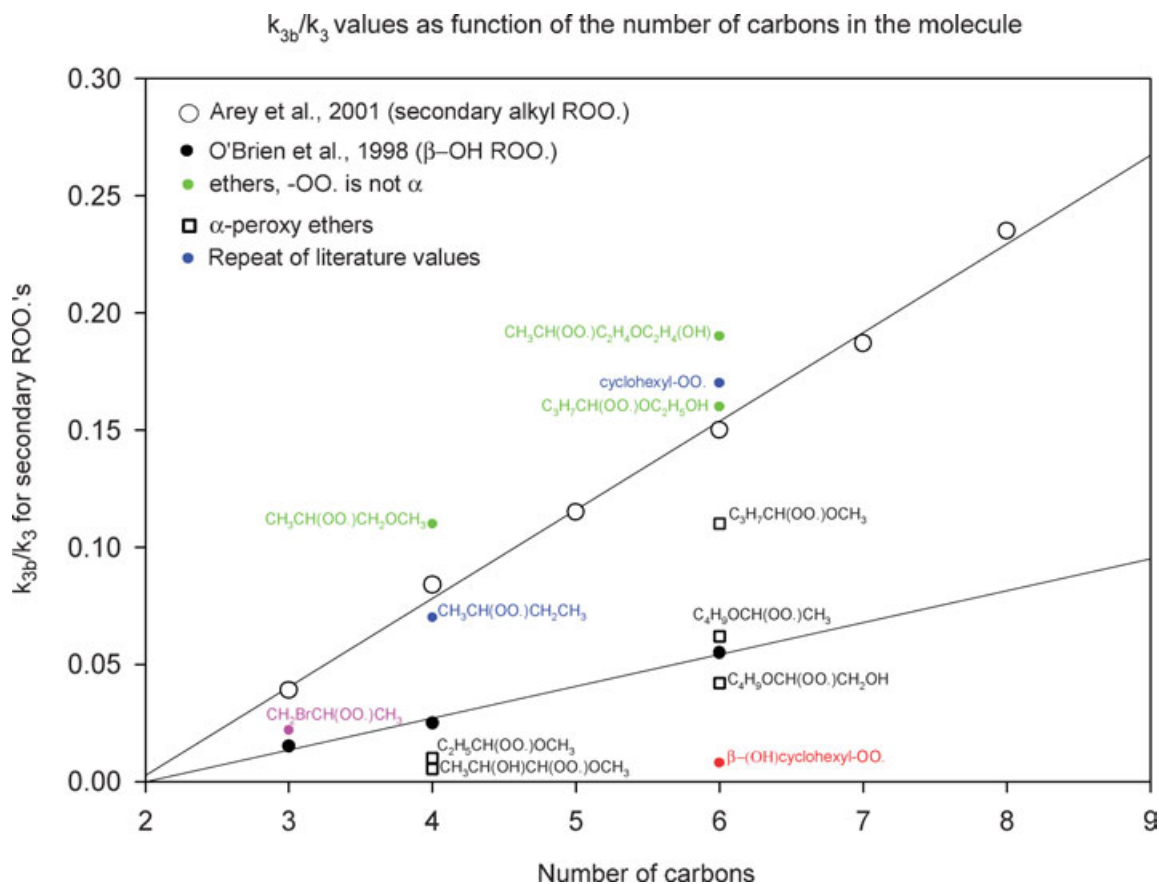


Figure 6 Summary of k_{3b}/k_3 values for secondary peroxy radicals.

radical, but we can calculate the oxygen atom stabilization as $0.54 = (0.15)(x^2)$, where 0.15 is the k_{3b}/k_3 value for secondary peroxy hexyl radicals and x is the stabilization factor, i.e. 1.9. This value for stabilization by an O-group substituent is also in fact not inconsistent with the results obtained to this point.

In the 2-butoxyethanol case, the total organic nitrate yield is greater than for ethyl butyl ether because the OH group will only decrease the branching ratio for the $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}(\text{OO}\cdot)\text{CH}_2(\text{OH})$ radicals, while acting to stabilize all other isomeric peroxy nitrites. In the 1-methoxy-2-propanol case, the OH group has a negative impact for all of the peroxy nitrite intermediates on the propyl side of the molecule, decreasing the total yield. We summarize in Tables II and III the impact of the —OR and —OH groups on branching ratios for compounds studied here.

CONCLUSIONS

We have reported measurements of the organic nitrate yields from OH oxidation of methoxy propane, 1-methoxy-2-propanol, ethoxybutane, and 2-butoxy-

ethanol in the presence of NO. Taken with existing data for simple butyl peroxy and hexyl peroxy radicals, our data show that the ether linkage decreases k_{3b}/k_3 values for peroxy nitrites that are α to the ether linkage. These k_{3b}/k_3 values were reduced by an average factor of 0.5 ± 0.3 for secondary peroxy nitrites α - to the —OR group, relative to unsubstituted secondary alkyl nitrites. This information is important to enable prediction of the ozone production potential of important atmospheric ethers, such as methyl t-butyl ether (MTBE).

We also determined the average heteroatom stabilization effect for both —OR and —OH groups. The average value for the heteroatom stabilization is $1.7 (\pm 0.4)$, meaning that peroxy radicals with oxygen substituents in positions β (for —O— groups), γ (for —OH groups), and farther from the oxygen-containing substituent had k_{3b}/k_3 values $1.7 (\pm 0.4)$ times that of the analogous alkyl peroxy nitrites. This can be compared to what has been found for other substituted alkyl peroxy nitrites. We found that the stabilization effect for Br atom substitution in the molecule is 1.45 [16], while it is 1.3 for an additional methylene group [14]. To effectively summarize what is known about substituent effects and the size of the R-OO· group, we

have plotted the k_{3b}/k_3 values for all secondary peroxy radicals determined by this group [16] and Arey et al. [14] in Fig. 6. It is clear from the summary presented in Fig. 2 that substituents, particularly those α - (or β - in the case of $-\text{OH}$) to the peroxy group, have a very large impact on the k_{3b}/k_3 values.

Understanding the effect of the oxygen substitution in these ethers and glycol ethers contributes to a better understanding of organic nitrate formation for complex oxygen-substituted VOCs, and thus the ozone formation potential of oxygenated VOCs and alkenes, since the peroxy radicals and the peroxy nitrite intermediates are oxygen substituted. Given their reactivities, oxygenated VOCs are very important contributors to ozone formation, and understanding the effect of the extra oxygen in the molecules will help further our understanding of ozone formation. Indeed, as discussed by numerous authors, in both rural/forested and urban environments, a majority of the reactive VOCs are either olefinic and thus react with OH via addition, or are already oxygen containing. It is particularly important that organic nitrate yields for aldehydes be determined. Given the new information about the surprising importance of organic nitrates to atmospheric odd nitrogen [32], much more information about organic nitrate yields as a function of structure and functional groups is needed.

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