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The atmospheric oxidation of diethyl ether: chemistry of the C_2H_5 -O-CH(O[•])CH₃ radical between 218 and 335 K

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The products of the Cl atom initiated oxidation of diethyl ether (DEE) were investigated at atmospheric pressure over a range of temperatures (218–335 K) and O_2 partial pressures (50–700 Torr), both in the presence and absence of NO_x. The major products observed at 298 K and below were ethyl formate and ethyl acetate, which accounted for $\approx 60-80\%$ of the reacted diethyl ether. In general, the yield of ethyl formate increased with increasing temperature, with decreasing O₂ partial pressure, and upon addition of NO to the reaction mixtures. The product yield data show that thermal decomposition reaction (3), $CH_3CH_2-O-CH(O^{\bullet})CH_3 \rightarrow CH_3CH_2-O-CH=O$ + CH₃, and reaction (6) with O₂, CH₃CH₂–O–CH(O[•])CH₃ + O₂ \rightarrow CH₃CH₂–O–C(=O)CH₃ + HO₂ are competing fates of the CH₃CH₂–O–CH(O[•])CH₃ radical, with a best estimate of $k_3/k_6 \approx$ $6.9 \times 10^{24} \exp(-3130/T)$. Thermal decomposition via C–H or C–O bond cleavage are at most minor contributors to the CH_3CH_2 -O- $CH(O^{\bullet})CH_3$ chemistry. The data also show that the CH_3CH_2 –O–CH(O•)CH₃ radical is subject to a chemical activation effect. When produced from the exothermic reaction of the CH₃CH₂-O-CH(OO[•])CH₃ radical with NO, prompt decomposition via both CH₃- and probably H-elimination occur, with yields of about 40% and \leq 15%, respectively. Finally, at temperatures slightly above ambient, evidence for a change in mechanism in the absence of NO_x , possibly due to chemistry involving the peroxy radical CH₃CH₂-O-CH(OO•)CH₃, is presented.

Introduction

Aliphatic ethers are present in the atmosphere due to their use as fuel additives and as solvents, and thus they can contribute to the formation of photochemical smog. Total global emissions of ethers from industrial sources are believed to be about 3.5 Tg yr^{-1} , with an additional 2 Tg yr^{-1} arising from biomass burning.¹ These species are generally more reactive in the atmosphere than alkanes of similar chain length, and have propensities for ozone production on urban and regional scales that are similar to or larger than alkanes of similar size.^{2,3}

Diethyl ether (DEE) is among the more common of the aliphatic ethers. Its major destruction pathway in the atmosphere is *via* reaction with OH. With typical urban [OH] levels exceeding 10^6 molecule cm⁻³ and $k_{OH} = 1.3 \times 10^{-11}$ cm³ molecule⁻¹ s^{-1,4} the atmospheric residence time of diethyl ether (and of most other aliphatic ethers) will be ≤ 1 day. The mechanism of the atmospheric oxidation of diethyl ether has been explored in the laboratory by three groups.⁵⁻⁷ The major product of the oxidation at 298 K in the presence of NO_x is ethyl formate, while lower yields of ethyl acetate and acetaldehyde have also been reported. The oxidation is thought to proceed predominantly *via* the formation of the 1-ethoxyethoxy radical, CH₃CH₂OCH(O[•])CH₃, following OH attack

at the -CH₂- groups in the parent ether:

$$\begin{array}{l} OH + CH_3CH_2OCH_2CH_3(+O_2) \\ \rightarrow CH_3CH_2OCH(OO^{\bullet})CH_3 \end{array} \tag{1}$$

$$\begin{array}{l} CH_{3}CH_{2}OCH(OO^{\bullet})CH_{3} + NO \\ \rightarrow CH_{3}CH_{2}OCH(O^{\bullet})CH_{3} + NO_{2} \end{array} \tag{2}$$

The observed products then originate from the decomposition of 1-ethoxyethoxy or its reaction with O_2 :

$$CH_3CH_2OCH(O^{\bullet})CH_3 \rightarrow CH_3CH_2OCH(=O) + CH_3^{\bullet}$$
(3)

$$CH_{3}CH_{2}OCH(O^{\bullet})CH_{3} \rightarrow CH_{3}CH_{2}OC(=O)CH_{3} + H^{\bullet}$$
(4)

$$CH_{3}CH_{2}OCH(O^{\bullet})CH_{3} \rightarrow CH_{3}CH_{2}O^{\bullet} + CH_{3}CH(=O)$$
(5)

$$CH_{3}CH_{2}OCH(O^{\bullet})CH_{3} + O_{2}$$

$$\rightarrow CH_{3}CH_{2}OC(=O)CH_{3} + HO_{2}$$
(6)

Further reactions of the ${}^{\bullet}CH_3$ radical will lead predominantly to formaldehyde, while the majority of the $CH_3CH_2O^{\bullet}$ radicals generated in reaction (5) will form additional acetaldehyde.

Wallington and Japar⁵ observed high yields of ethyl formate in their chamber studies of diethyl ether oxidation in air in the presence of NO_x; a 92 \pm 6% yield from the OH-initiated oxidation and a 87 \pm 6% yield from the Cl atom initiated

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oxidation were reported. Ethyl acetate and acetaldehyde were not detected (yields both <5%), and the authors concluded that decomposition pathway (3) dominated the chemistry of 1-ethoxyethoxy under ambient conditions. Eberhard et al.⁶ also reported large yields of ethyl formate in their studies of the OHinitiated oxidation of diethyl ether in air at 298 K, but also detected minor yields of ethyl acetate and acetaldehyde. Their data indicated that pathways (3), (5), and (6) were occurring with respective yields of $66 \pm 14\%$, $8 \pm 2\%$, and $4 \pm 3\%$ per 1-ethoxyethoxy formed. The product yield data of Cheema et al^{7} in air in the presence of NO_x are consistent with those reported earlier (65 \pm 5% ethyl formate yield, 13 \pm 5% acetaldehyde yield, and 7 \pm 3% ethyl acetate yield from the OH-initiated oxidation; $79 \pm 9\%$ ethyl formate yield, $11 \pm 3\%$ acetaldehyde yield, $7 \pm 1\%$ ethyl acetate yield from the Cl-atom initiated oxidation), confirming the dominance of reaction (3) in air at 298 K. However, these workers also studied the O2 dependence of the product yields, and found the data to be inconsistent with the exclusive occurrence of reaction (3), (5), and (6). More specifically, the yield of ethyl acetate did not change dramatically with O₂ and did not tend to zero at low O₂ as would be expected if reaction (6) were its sole source. Cheema et $al.^{7}$ thus postulated the occurrence of reaction (4), H-atom elimination from 1-ethoxyethoxy, an O2-independent source of ethyl acetate. While not a common occurrence in unsubstituted alkoxy radical chemistry, H-atom elimination from alkoxy radicals of structure similar to 1-ethoxyethoxy, HOCH₂O• and $CH_3OCH_2O^{\bullet}$, has also been identified and characterized.⁸⁻¹⁰

Using structure–additivity relationships, decomposition reactions (3) and (4) are expected to be exothermic and roughly thermoneutral,⁷ respectively, and thus likely occur with reasonably small barriers, ≤ 10 kcal mol⁻¹ or so.^{7,10} Previous work from this lab and elsewhere has shown that chemical activation can play a role in determining product yields in these circumstances.¹¹ When produced from the exothermic reaction of peroxy radicals with NO, alkoxy radicals are generated with internal excitation. In cases where the barrier to unimolecular reaction is low, this internal energy may exceed the barrier height and allow for "prompt" or activated decomposition.

With the specific goal of investigating the effects of chemical activation on 1-ethoxyethoxy radical chemistry and more closely examining the origin of the ethyl acetate product and the nature of the H-atom elimination pathway (4), we report in this work a study of the Cl-atom initiated oxidation of diethyl ether both in the presence and absence of NO_x , and as a function of both the O_2 partial pressure (50–700 Torr) and temperature (218–335 K). The data clearly support the occurrence of activated elimination of CH₃– from 1-ethoxyethoxy in the presence of NO_x , and indicate that activated H-atom elimination is also likely occurring. Relative rate coefficients for reactions (3) and (6) as a function of temperature are also reported, along with upper limits for the rate coefficients for reactions (4) and (5).

Experimental

Experiments were carried out in a 2 m long, 47 L evacuable stainless steel environmental chamber that has been described

previously.^{12,13} Briefly, quantification of starting material and products is accomplished using a Fourier Transform spectrometer (Bomem DA3.01) operating in the infrared. The spectrometer is interfaced to the chamber *via* a set of Hanst-type multipass optics, which provide an observational pathlength of 32.6 m. Infrared spectra covered the range 800–3900 cm⁻¹, and were obtained at a resolution of 1 cm⁻¹ from the coaddition of 200 scans (acquisition time 3–4 min). The temperature of the cell was regulated by flowing either ethanol (T < 298 K) or water (T > 298 K) from a circulating bath through a jacket surrounding the cell. The chamber temperature was monitored using six thermocouple gauges located along its length, and was found to be uniform along the length of the cell to within ±1 K.

Experiments were conducted using mixtures of Cl₂ (1.4- 3.5×10^{15} molecule cm⁻³), diethyl ether (2–7 × 10¹⁴ molecule cm⁻³), and NO (0–14 \times 10¹⁴ molecule cm⁻³) in 750 \pm 20 Torr of O_2/N_2 diluent, at temperatures ranging from 218 to 335 K. The O₂ partial pressure was varied between 50 and 700 Torr. The O₂ was added directly to the chamber, while minor components were flushed into the chamber from smaller calibrated volumes using a flow of N₂. A Xe arc lamp, directed along the length of the chamber and filtered to provide radiation in the 240-400 nm range, was used to photolyze Cl₂ and thus initiate the chemistry. Mixtures were photolyzed for 4-6 periods, each of duration 20-40 s, and an infrared spectrum was recorded after each photolysis period (with the Xe arc lamp blocked). Ouantification of diethyl ether and its oxidation products was carried out using commercial spectral stripping routines. The major products, ethyl formate and ethyl acetate, were quantified under all conditions studied using reference spectra recorded in-house at the temperature at which the experiments were conducted. Quantification of minor products was carried out using either reference spectra recorded in-house at or near the temperature under study (CH₂O, CH₃OH), via integration of spectral bands and comparison with integrated band intensities measured near 298 K (the peroxynitrate C₂H₅OCH(OONO₂)CH₃), or via comparison with reference spectra obtained near room temperature (CH₃ONO, CH₃ONO₂, and formic acid).

Reaction of Cl atoms with diethyl ether is very rapid, $k \approx$ 2.5×10^{-10} cm³ molecule⁻¹ s⁻¹,¹⁴ and is thus significantly more rapid (by a factor of 3-1000) than reaction of Cl with all identified reaction products. Thus, consumption of products via Cl atom reaction was of minimal concern. Correction of measured product concentrations for loss via Cl atom reaction was not necessary (<2%) for most products (ethyl formate, ethyl acetate, methyl nitrate, methyl nitrite, and formic acid), while consumption of formaldehyde and methanol by Cl atom reaction was about 7-12% at the end of a typical experiment (approx. 50% conversion of the parent diethyl ether). Unless otherwise stated, formaldehyde and methanol concentrations and yields given below are those obtained after correction for Cl atom consumption. Control experiments showed that loss of DEE or major reaction products via either photolysis or heterogeneous reaction on the chamber surfaces was negligible.

Chemicals used in these experiments were obtained from the following sources: Cl_2 (Matheson, UHP); diethyl ether, ethyl formate, ethyl acetate (Sigma-Aldrich); O_2 (US Welding); N_2 ,

(boil-off from liquid N_2 , US Welding). Gaseous starting materials (Cl₂ and NO) were used as received, while liquids (diethyl ether, ethyl formate and ethyl acetate) were subjected to several freeze-pump-thaw cycles before use.

Results and discussion

In all experiments, oxidation of diethyl ether was initiated *via* reaction with Cl atoms produced from the photolysis of Cl₂. Reaction of Cl with diethyl ether can occur at two sites, with reaction at the $-CH_2$ - groups likely to dominate:

(

$$Cl_2 \rightarrow Cl + Cl$$
 (7)

$$Cl + CH_3CH_2OCH_2CH_3(+O_2) \rightarrow CH_3CH_2OCH(OO^{\bullet})CH_3 + HCl$$
(8)

If it is assumed that ethyl formate and ethyl acetate are predominantly generated following reaction (8), it follows that most (>80%) of the Cl atom attack occurs at the CH₂ site.^{5–7} However, the possibility of ethyl formate production from reaction at the CH₃ groups must also be considered. Cl atom attack at the –CH₃ groups will lead in part to the CH₃CH₂OCH₂CH₂O[•] radical, whose likely fate is decomposition reaction (9), leading to ethyl formate, or isomerization reaction (10):

$$\begin{array}{l} CH_{3}CH_{2}OCH_{2}CH_{2}O^{\bullet}(+O_{2})\\ \rightarrow CH_{3}CH_{2}OCH_{2}O_{2}+CH_{2}O \end{array} \tag{9}$$

$$\begin{array}{l} CH_{3}CH_{2}OCH_{2}O_{2} \rightarrow \rightarrow CH_{3}CH_{2}OCHO, \text{ other products}\\ \\ CH_{3}CH_{2}OCH_{2}CH_{2}O^{\bullet}(+O_{2}) \rightarrow CH_{3}CH(OO^{\bullet})OCH_{2}CH_{2}OH\\ \end{array} \tag{10}$$

A computational study by Ferenac *et al.*¹⁵ has shown that isomerization of the related $CH_3OCH_2CH_2O^{\circ}$ species is a very low-barrier process, and isomerization reaction (10) of $CH_3CH_2OCH_2CH_2O^{\bullet}$ is expected to be even more facile. However, their computations also suggest that decomposition of $CH_3OCH_2CH_2O^{\bullet}$, and hence of $CH_3CH_2OCH_2CH_2O^{\bullet}$, is also facile and cannot be ruled out as a significant process. The lower barrier to isomerization would point to increasing importance of isomerization (10) versus decomposition (9) as temperature is decreased. End-products of the isomerization are not known, but likely include multi-functional species such as $HC(O)OCH_2CH_2OH$ and $CH_3CH(OH)OCH_2CHO$ (all conditions), and $CH_3C(O)OCH_2CH_2OH$ and $CH_3CH(OOH)$ - OCH_2CH_2OH (in the absence of NO_x only).

Experimental results will be presented in three sections. Data obtained in the absence of NO (218, 232, 251, 269, and 298 K) will first be discussed, followed by those obtained with NO added to the reaction mixtures (232, 251, 269, and 298 K). Lastly, anomalous behavior observed in a limited set of experiments carried out at 335 K will be described. In initial discussions, it is assumed that all observed ethyl formate and ethyl acetate derive from attack at the $-CH_2$ - group, reaction (8). The effects of a possible minor contribution to ethyl formate production *via* attack at the CH_3 groups will be discussed in section 2.

1. Experiments conducted without NO_x, 298 K and below

Products identified following the photolysis of mixtures of Cl_2 and diethyl ether in O_2/N_2 diluent (*i.e.*, in the absence of NO_x) at all temperatures studied (298, 269, 251, 232 and 218 K) were ethyl formate, ethyl acetate, formaldehyde and methanol. In addition, formic acid was also observed at 298, 269 and 251 K.

Product concentrations observed as a function of diethyl ether consumption are shown in Fig. 1 for an experiment carried out in 1 atm synthetic air at 269 K. The observed products are consistent with the basics of the established mechanism, reactions (7), (8), (11) and (12), followed by reactions (3) through (6).

$$2 \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{OCH}(\operatorname{OO}^{\bullet})\operatorname{CH}_{3} \rightarrow 2 \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{OCH}(\operatorname{O}^{\bullet})\operatorname{CH}_{3} + \operatorname{O}_{2}$$
(11a)

$$2 \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{OCH}(\operatorname{OO}^{\bullet})\operatorname{CH}_{3} \rightarrow \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{OCH}(\operatorname{OH})\operatorname{CH}_{3} + \operatorname{CH}_{3}\operatorname{CH}_{2}\operatorname{OC}(=\operatorname{O})\operatorname{CH}_{3} + \operatorname{O}_{2}$$
(11b)

$$\begin{array}{l} CH_{3}CH_{2}OCH(OO^{\bullet})CH_{3} + HO_{2} \\ \rightarrow CH_{3}CH_{2}OCH(OOH)CH_{3} + O_{2} \end{array} \tag{12a}$$

$$\begin{array}{l} CH_3CH_2OCH(OO^{\bullet})CH_3 + HO_2 \\ \rightarrow CH_3CH_2OC(=O)CH_3 + H_2O + O_2 \end{array} \tag{12b}$$

Self-reaction (11) of the 1-ethoxyethylperoxy radical (or reaction of this species with other peroxy radicals, *e.g.*, CH₃O₂) is expected to lead to the formation of both molecular (ethyl acetate, and 1-ethoxyethanol) and radical (1-ethoxyethoxy, CH₃CH₂OCH(O•)CH₃) products. Additional ethyl acetate can then be generated from the reaction (6) of O₂ with the 1-ethoxyethoxy radical, and potentially from the H-atom elimination from 1-ethoxyethoxy, reaction (4). Ethyl formate results from methyl radical elimination from the 1-ethoxyethoxy radical, reaction (3). On a molar basis, the two ester products, ethyl formate and ethyl acetate, account for 79 ± 5% of the reacted diethyl ether in the experiment shown in



Fig. 1 Observed (uncorrected) product concentrations versus DEE consumption following photolysis of a mixture of Cl₂ (35×10^{14} molecule cm⁻³)/DEE (7×10^{14} molecule cm⁻³)/O₂ (150 Torr)/N₂ (610 Torr) at 269 K. Filled squares–ethyl acetate; filled triangles–formalde-hyde; filled circles–formic acid; open circles–ethyl formate; open diamonds–methanol. Solid lines are linear least squares fits to the data.

Fig. 1. The remaining observed products (formaldehyde, methanol and formic acid) are all end-products of the oxidation of the methyl radical product of reaction (3), *e.g.*,:

 $\begin{array}{l} \mathrm{CH_3O_2+CH_3O_2} \rightarrow \mathrm{CH_3O+CH_3O+O_2} \\ \\ \mathrm{CH_3O_2+CH_3O_2} \rightarrow \mathrm{CH_3OH+CH_2O+O_2} \\ \\ \mathrm{CH_3O+O_2} \rightarrow \mathrm{CH_2O} \ + \ \mathrm{HO_2} \\ \\ \\ \mathrm{HO_2+CH_2O} \leftrightarrow \mathrm{HOCH_2OO} \\ \\ \\ \\ \mathrm{HOCH_2OO} \rightarrow \rightarrow \mathrm{HCOOH} \\ \\ \\ \mathrm{CH_3O_2+HO_2} \rightarrow \mathrm{CH_3OOH} \ + \ \mathrm{O_2} \end{array}$

Note that, for the data shown in Fig. 1, the concentrations of the three products derived from the CH₃ radical, after correction for secondary consumption *via* reaction with Cl, sums to $92 \pm 10\%$ of the ethyl formate yield. Values of 70–90% were typical at 298, 269 and 251 K; lower values were found at lower temperature, where ethyl formate yields were low and co-products were often not detectable. The slight shortfall relative to the ethyl formate yield at the higher temperatures may be the result of the formation of CH₃OOH and its subsequent loss to the chamber walls.

In addition to absorption bands due to the products just discussed, unidentified absorption features at approximately 950, 1050, 1130, 1230, 1345, 1380, 1740 and 1780 cm⁻¹ were clearly observed in experiments conducted above 250 K. It is possible that some of these bands belong to the expected product of reaction (11b), 1-ethoxyethanol, CH₃CH₂O-CH(OH)CH₃. While a spectrum of this species could not be found, and samples do not appear to be available commercially, we note that structurally similar molecules (e.g., dimethoxymethane, 2-ethoxyethanol) possess some bands in common with those observed. For example, dimethoxymethane possesses strong absorption features at 935, 1050, and 1140 cm⁻¹.16 On average, the identified products (ethyl formate, ethyl acetate, formaldehyde, methanol and formic acid) accounted for $79 \pm 12\%$ of the reacted carbon at 269 K. Mass balances at other temperature (298, 251, 232, 218 K) were typically somewhat lower, but always in excess of 60%. For the lower temperatures, some of the reduced mass balance was due to the fact that some products were sometimes (CH₃OH, CH₂O) or always (formic acid) formed in undetectable amounts, particularly when ethyl formate yields were low. Furthermore, given that it is likely that about 30-50% of the total product in these experiments is ethyl acetate derived from the molecular channels of reactions of CH₃CH₂O-CH(OO•)CH₃ radical (either directly or via secondary conversion of 1-ethoxyethanol), it can be expected that the 1ethoxyethanol accounts for a large fraction of the remaining carbon.

As noted in the introduction, acetaldehyde has been identified as a product of diethyl ether oxidation by some workers, and has been attributed to the occurrence of reaction (5). No conclusive evidence for acetaldehyde could be found in any of the spectra obtained in this work. However, acetaldehyde is a rather weak IR absorber and its most intense absorption feature, centered at 1745 cm⁻¹, overlaps with numerous other carbonyl-containing products generated in these experiments. Thus, yields as high as 15% at 296 and 269 K would have been undetectable under the experimental conditions used herein. Conditions typically used in lower temperature experiments (lower diethyl ether concentrations) were such that a less stringent upper limit, 20–25%, could be established; however, thermodynamic considerations suggest strongly that process (5) will possess a higher energy barrier than reaction (3) and thus is unlikely to occur to a significant extent, especially at reduced temperature. Given that two acetaldehyde molecules are generated for every occurrence of reaction (5), it seems reasonable to conclude that this reaction contributes <10% to the chemistry over the entire 218–298 K temperature range.

Experiments carried out in the absence of NO should be devoid of any chemical activation effects, and thus are well suited to the study of the chemistry of thermalized 1-ethoxyethoxy radical, i.e., the competition between its thermal decomposition via reactions (3), (4) and/or (5) and its reaction with O₂, reaction (6). Thus, experiments were carried out over a range of temperatures (218–298 K), with the O₂ partial pressure varied between 50 and 700 Torr at each temperature. As an example, yields of the two main products, ethyl acetate and ethyl formate, as a function of O₂ partial pressure at 269 K are shown as the open symbols in Fig. 2. The entire dataset (218-298 K; 50-700 Torr O₂) is summarized in a more compact form, as ratios of the vield of ethyl formate to the total (ethyl formate + ethyl acetate) yield, in Table 1a and in Fig. 3. Note that uncertainties in individual ester yields are typically $\pm 7\%$ (including uncertainty in spectral analysis, and potential systematic uncertainty in the concentration of reference samples). This leads to an uncertainty of $\pm (0.03 \text{ to } 0.05)$ for the product ratios given in Table 1 (i.e., those obtained with and without NO_{y}).

A more quantitative treatment of these data is given below, but a number of initial observations can be made from the dataset. First, the sum of the yields of the two esters is roughly



Fig. 2 Fractional molar yields of ethyl formate (triangles) and ethyl acetate (circles) as a function of O_2 partial pressure at 269 K, both in the presence (filled symbols) and absence (open) of NO_x. Solid lines represent fits to the data using parameters given in column two (no NO_x) and column three (with NO_x) of Table 2.



Fig. 3 Yield ratios, Y(EF)/[Y(EF) + Y(EA)], obtained in the absence of NO_x as a function of O₂ partial pressure and temperature (solid squares, 298 K; open triangles, 269 K; filled triangles, 251 K; open circles, 232 K; closed circles, 218 K). Solid lines, yield ratios obtained using the parameters derived from a fit to all data obtained in the absence of NO_x (column two of Table 2). Dashed lines, yield ratios obtained between 232 and 298 K (with and without NO_x, column four of Table 2). See text for details.

constant at a given temperature, but shows a slight decrease with decreasing temperature. Secondly, at a given temperature, the yield of ethyl formate decreases with increasing O_2 , while the yield of ethyl acetate increases, consistent with competition between the O_2 -dependent production of ethyl acetate *via* reaction (6) and ethyl formate production *via* thermal decomposition of 1-ethoxyethoxy radical, reaction (3). Third, intercepts less than unity in Fig. 3 indicate that there is a rather larger O_2 -independent source of ethyl acetate in these experiments, which increases with decreasing temperature. This likely results from reaction of CH₃CH₂O-CH(OO•)CH₃ radicals with themselves or with other organic peroxy radicals present in the system, but could also include a contribution from reaction (4).

Assuming that the chemistry is dominated by reactions (7), (8), (11) and (12) and reactions (3), (4) and (6), the product ratio discussed above (and presented in Fig. 3) is determined by the following expression:

$$Y(EF)/[Y(EF) + Y(EA)] = [(S - I)/S] \times [k_3/(k_3 + k_4 + k_6[O_2])]$$
(A)

where Y(EF) and Y(EA) are the fractional molar yields of ethyl formate and ethyl acetate, respectively; *S* is the sum of the fractional yields of the two ester species; *I* is the fractional yield of ethyl acetate resulting from molecular channels of peroxy radical self- and cross-reactions (the intercept of the ethyl acetate data shown in Fig. 2); k_3 and k_4 are the first order rate coefficients for reactions (3) and (4); and k_6 is the secondorder rate coefficient for reaction (6).

Fits of expression (A) to the data can then be used to draw conclusions regarding the relative rates of the sources of ethyl formate (reaction (3)) and of ethyl acetate (reactions (4), (6)

Table 1 (a) Ethyl formate and ethyl acetate yields from DEE oxidation in the absence of NO_x over a range of temperatures and O_2 partial pressures. Data are given as Y(EF)/[Y(EF) + Y(EA)], where Y(EF)and Y(EA) are, respectively, fractional yields of ethyl formate and ethyl acetate. (b) Ethyl formate and ethyl acetate yields from DEE oxidation in the presence of NO_x over a range of temperatures and O_2 partial pressures. Data are given as Y(EF)/[Y(EF) + Y(EA)], where Y(EF) and Y(EA) are, respectively, yields of ethyl formate and ethyl acetate

(a) O ₂ partial pressure/	A 10 H	222 V	0.51 W	2 (0) 1	2 00 1	
Torr	218 K	232 K	251 K	269 K	298 I	K 335 K
50	0.21	0.30	0.42	0.49	0.59	0.61
150	0.11	0.22	0.36	0.47	0.57	0.60
250				0.43		
300		0.18	0.30		0.55	0.56
350				0.41		
400	0.07					
425				0.40		
450			0.25		0.53	0.55
475				0.39		
500		0.13				
600			0.23	0.36	0.51	0.55
700	0.05	0.12		0.35		
(b)						
O ₂ partial pressure/						
Torr	232 K	251 K	269	K 29	8 K 3	335 K
50	0.72	0.79	0.85	0.8	8 ().88
150	0.63	0.74	0.83	0.8	9 ().87
250	0.02	0.7.1	0.80	0.0		,
300	0.57	0.68				
350			0.78	0.8	5	
450		0.61			().87
475			0.76			
500	0.52					

and/or 11b) as a function of temperature. Note that the occurrence of reaction (5) will have no impact on the fits. In initial attempts to fit the dataset of Fig. 3 to equation (A), it was found that separation of the contribution of the three potential components to ethyl acetate formation (the intercept I, k_4 , and $k_6[O_2]$) was not possible; essentially, a trade-off exists in which the ethyl acetate produced from reaction (4) is balanced in the fits by that produced from the RO_2 -RO₂ chemistry (the parameter I in equation (A)). Thus, similar quality fits could be achieved with $k_4 \approx 0$ as with k_4 approaching the value for k_3 .

0.59

0.51

0.73

0.71

0.83

0.86

600

700

However, a strong case can be made in favor of a rather small value for k_4 relative to k_3 . Firstly, in experiments conducted in the presence of NO_x (see Section 2 below), yields of ethyl acetate are greatly reduced and analysis of the data shows that $k_4 \leq (0.25 \text{ to } 0.3) * k_3$. A more stringent constraint on the magnitude of k_4 can probably be obtained from a consideration of the nature of the two processes, elimination of an H-atom in reaction (4) *versus* elimination of a CH₃ group in reaction (3).^{11,17,18} Reaction (3) will be favored for two reasons, because it is likely more exothermic than reaction (4), and because CH₃ is a better "leaving group" than is H-atom. It is thus likely that the two reactions will have similar *A*factors, but that the activation energy for reaction (4) will

Table 2 Rate coefficient ratio k_3/k_6 (molecule cm⁻³) versus temperature, as derived from various fits to the data

Temp./K	Global Fit, no NO_x^a	Global Fit, with $NO_x^{\ b}$	Simultaneous Fit of all data ^c
298	1.53×10^{20}	1.40×10^{20}	1.89×10^{20}
269	5.7×10^{19}	3.4×10^{19}	6.0×10^{19}
251	2.8×10^{19}	1.2×10^{19}	2.6×10^{19}
232	1.2×10^{19}	3.4×10^{18}	9.5×10^{18}
218	5.4×10^{18}		4.0×10^{18}
A-factor	1.3×10^{24}	7.0×10^{25}	6.9×10^{24}
Activation	2700	3910	3130
Temp./K			

^{*a*} Data derived from a fit of all data (218–298 K) obtained in the absence of NO_x to equation (A), see text for details. ^{*b*} Data derived from a fit of all data obtained in the presence of NO_x (232–298 K) to equation (B), see text for details. ^{*c*} Data derived from the simultaneous fit of all data obtained between 232–298 K with and without NO_x present, see text for details.

exceed that for reaction (3), by at least 2-3 kcal mol⁻¹ and likely by considerably more. Note that even a 2 kcal mol⁻¹ difference in activation energies for the two processes implies a 30-100 times difference in rate for the temperature range investigated herein.^{11,17,18}

Thus, for initial consideration it was assumed that k_4 was negligibly small. A fit of the data to equation (A) was then conducted using the entire NO_x-free dataset (218 through 298 K) simultaneously, with k_4 fixed to zero, and I and k_3/k_6 each parameterized by a function of the form $A \exp(-B/T)$, where A and B are fit parameters and T is the temperature. A rate coefficient ratio $k_3/k_6 = 1.3 \times 10^{24} \exp(-2690/T)$ molecule cm⁻³ was obtained. Calculated yield curves are shown as solid lines in Fig. 3, and retrieved values for k_3/k_6 are summarized in Table 2 and in Fig. 4. To examine the



Fig. 4 Rate coefficient ratios, k_3/k_6 , plotted in Arrhenius form. Filled circles $-k_3/k_6$ values obtained using the parameters derived from a fit to all data obtained in the absence of NO_x (column two of Table 2). Open circles $-k_3/k_6$ values obtained using the parameters derived from a fit to all data obtained in the presence of NO_x (column three of Table 2). Solid line $-k_3/k_6$ values obtained using parameters derived from a fit to all data obtained between 232 and 298 K (with and without NO_x, column four of Table 2).

possible (but unlikely) effect of a non-negligible occurrence of k_4 , a fit was carried out with the *A*-factor for reaction (4) set equal to that for reaction (3), but with the activation energy increased by 0.6 kcal mol⁻¹ (to mimic the $k_4 \leq (0.25 \text{ to } 0.3) * k_3$ constraint discussed above). This fitting procedure yields a similar expression, $k_3/k_6 = 9.1 \times 10^{23} \exp(-2620/T)$ molecule cm⁻³, which returns k_3/k_6 values that are 4–13% lower than the those obtained from the fit conducted with $k_4 = 0$. A more thorough discussion of the relative rates of processes (3), (4) and (6) will be presented later. However, it is apparent that, while the value of k_3/k_6 changes by more than an order of magnitude between 218 and 298 K, the activation energy for reaction (3) is rather low for an alkoxy radical decomposition reaction.

2. Experiments conducted in the presence of NO_x , 298 K and below

Experiments were also conducted in the presence of NO_x over a range of temperatures (232–298 K) and O_2 partial pressures (50–700 Torr). The expected chemistry^{5–7} is as follows:

$$\begin{array}{l} Cl \ + \ CH_3CH_2OCH_2CH_3(+O_2) \\ \rightarrow CH_3CH_2OCH(OO^{\bullet})CH_3 \ + \ HCl \end{array} \tag{8}$$

$$\begin{array}{l} CH_{3}CH_{2}OCH(OO^{\bullet})CH_{3} + NO\\ \rightarrow CH_{3}CH_{2}OCH(O^{\bullet})CH_{3} + NO_{2} \end{array} \tag{2a}$$

$$\begin{array}{ll} CH_{3}CH_{2}OCH(OO^{\bullet})CH_{3}\,+\,NO\\ \rightarrow CH_{3}CH_{2}OCH(ONO_{2})CH_{3} \end{array} \tag{2b}$$

$$\begin{array}{l} CH_{3}CH_{2}OCH(OO^{\bullet})CH_{3}+NO_{2} \\ \rightarrow CH_{3}CH_{2}OCH(OONO_{2})CH_{3} \end{array} \tag{13}$$

$$CH_3CH_2OCH(O^{\bullet})CH_3 \rightarrow CH_3CH_2OCH(=O) + CH_3$$
(3)

$$CH_3CH_2OCH(O^{\bullet})CH_3 \rightarrow CH_3CH_2OC(=O)CH_3 + H$$
(4)

$$CH_{3}CH_{2}OCH(O^{\bullet})CH_{3} \rightarrow CH_{3}CH_{2}O^{\bullet} + CH_{3}CH(=O)$$
(5)

$$CH_{3}CH_{2}OCH(O^{\bullet})CH_{3} + O_{2}$$

$$\rightarrow CH_{3}CH_{2}OC(=O)CH_{3} + HO_{2}$$
(6)

OH radicals will also be generated in the presence of NO_x , *via* reaction of HO₂ with NO. However, box model (Acuchem)¹⁹ simulations showed that only a small fraction (5–35%) of the ether oxidation will be initiated by OH for conditions employed in this study. Products observed at all temperatures (highlighted in bold above) were ethyl formate, ethyl acetate, formaldehyde, methyl nitrite, methyl nitrate, peroxynitrates [assumed to be mostly CH₃CH₂OCH(OONO₂)CH₃], and an absorption band near 1285 cm⁻¹ consistent with the formation of organic nitrate(s) other than methyl nitrate.



Fig. 5 Infrared spectrum attributed to the peroxynitrate species, $CH_3CH_2OCH(OONO_2)CH_3$, formed following the photolysis of $Cl_2/DEE/NO_2$ mixtures in O_2/N_2 diluent at 269 K. Absorption cross sections obtained assuming quantitative conversion of DEE to the peroxynitrate.

Specific experiments were conducted to characterize and quantify the peroxynitrate, *via* the photolysis of mixtures of Cl_2 , diethyl ether, and NO_2 in air:

$$\begin{array}{l} \text{Cl} + \text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3(+\text{O}_2) \\ \rightarrow \text{CH}_3\text{CH}_2\text{OCH}(\text{OO}^{\bullet})\text{CH}_3 + \text{HCl} \end{array} (8)$$

$$\begin{array}{ll} CH_{3}CH_{2}OCH(OO^{\bullet})CH_{3}+NO_{2}\\ \rightarrow CH_{3}CH_{2}OCH(OONO_{2})CH_{3} \end{array} \tag{13}$$

A residual spectrum (obtained following subtraction of absorption features due to diethyl ether and NO₂) in an experiment at 269 K is shown in Fig. 5. Assuming stoichiometric conversion of diethyl ether to the peroxynitrate, absorption cross sections of 1.6×10^{-18} cm² molecule⁻¹ and 3.4×10^{-18} cm² molecule⁻¹ are obtained for the characteristic peroxynitrate features at 1295 cm⁻¹ and 1717 cm⁻¹, respectively. Quantification of peroxynitrate production in Cl₂/diethyl ether/NO photolysis experiments was carried out using either peroxynitrate standard spectra generated at specific temperatures as just described, or using integrated bandstrengths obtained using the data in Fig. 5. In all yield data reported below, diethyl ether consumption is corrected for the formation of the peroxynitrate-that is, product yields are calculated relative to the difference between the amount of diethyl ether consumed and the amount of peroxynitrate produced.

Following subtraction of spectra due to methyl nitrate and the peroxynitrate, as well as other products, residual absorption was observed at 1285 cm⁻¹. This absorption is consistent with organic nitrate formation in the system *via* reaction of peroxy radicals with NO, *e.g.*,

$$CH_{3}CH_{2}OCH(OO^{\bullet})CH_{3} + NO \rightarrow CH_{3}CH_{2}OCH(ONO_{2})CH_{3}$$
(2b)

Assuming a peak absorption cross section of 1.3×10^{-18} cm² molecule⁻¹ for the 1285 cm⁻¹ band (on the basis of data obtained in our laboratory), the yield of nitrate was found to be $6 \pm 2\%$ at 298 K and $8 \pm 3\%$ at 269 K. Nitrate yields at



Fig. 6 Observed (uncorrected) product concentrations versus consumption of DEE following photolysis of a mixture of Cl_2 (32×10^{14} molecule cm⁻³)/DEE (6.5×10^{14} molecule cm⁻³)/NO (14×10^{14} molecule cm⁻³)/O₂ (150 Torr)/N₂ (610 Torr) at 269 K. Filled circles – ethyl formate; open squares – sum of formaldehyde, methyl nitrite, and methyl nitrate; open diamonds, methyl nitrite; open circles – methyl nitrate; solid squares – formaldehyde; solid triangles – ethyl acetate. Solid lines – linear least squares fit to the ethyl formate and ethyl acetate data.

reduced temperatures were difficult to assess due to the increased contribution of the peroxynitrate to the measured absorption near 1300 cm⁻¹. These data should strictly be considered an upper limit to the actual CH₃CH₂OCH-(ONO₂)CH₃ yield, given the possible contribution of other species to the measured absorption. It is noteworthy that the nitrate yield at 298 K is measurably less than that obtained in the comparable 2-pentylperoxy + NO reaction.²⁰ The low nitrate yield is also consistent with the findings of Eberhard *et al.*,⁶ who found no evidence for production of CH₃CH₂O-CH(ONO₂)CH₃ in their study.

Observed product concentrations versus DEE consumption (corrected for peroxynitrate formation) for experiments carried out at 269 K in the presence of NO_x at an O_2 partial pressure of 150 Torr (total pressure 750 Torr) are shown in Fig. 6. Mass balance in experiments conducted at 269 K were on average $89 \pm 9\%$, indicating that essentially all products are identified. Mass balances at other temperatures (298, 251 and 232 K) were slightly lower, about 80%. Methyl radicals formed in the presence of NO_x are converted to formaldehyde, methyl nitrite or methyl nitrate. Note that in the data of Fig. 6, the sum of the observed concentrations of these three species is essentially identical to that of ethyl formate. Furthermore, under the conditions of highest NO_x $(>1 \times 10^{15} \text{ molecule cm}^{-3})$ and lowest O₂ (50 Torr), the sum of the CH₃ONO and CH₃ONO₂ concentrations exceeded the CH₂O concentration by a factor of 4.5–7.5; this result, coupled with model studies of the system, indicates that the predominant (>90%) co-product of ethyl formate was methyl radical (from reaction (3) following initial attack at the $-CH_2$ groups) rather than CH₂O itself (from reaction (9) following attack at the $-CH_3$ groups). That is, the vast majority of the ethyl formate is derived from attack at the CH₂ sites. The ratio of the sum of the concentrations of the three methyl-derived



Fig. 7 Yield ratios, Y(EF)/[Y(EF) + Y(EA)], obtained in the presence of NO_x as a function of O₂ partial pressure and temperature (filled squares, 335 K; open circles, 298 K; filled circles, 269 K; open squares, 251 K; filled triangles, 232 K). Solid line, yield ratios obtained using the parameters derived from a fit to all data obtained in the presence of NO_x (column three of Table 2). Dashed line, yield ratios obtained between 232 and 298 K (with and without NO_x, column four of Table 2). See text for details.

products to the ethyl formate concentration was typically 85–105% at 298 and 269 K. Ratios at lower temperature were generally lower and more scattered, owing largely to difficulty in detecting methyl nitrite under conditions where the ethyl formate yield is low. The complexity of the spectra in the 1700–1800 cm⁻¹ region, due to the presence of the two esters, formaldehyde and the peroxynitrate made identification and quantification of acetaldehyde difficult. Nevertheless, no evidence for this species was observed in any of the experiments conducted with NO_x present, and a yield of <20% is estimated.

Experiments with NO_x present were carried out over a range of temperatures (232, 251, 269, and 298 K) and O₂ partial pressures (50-700 Torr), largely to examine effects of chemical activation on the observed product yields. Ethyl formate and ethyl acetate yields were again used as the main diagnostics. As an example, molar yields of these two products are shown as a function of O₂ partial pressure at 269 K in Fig. 2. The entire dataset is shown in condensed form (as the ratio of the ethyl formate yield to the sum of the yields of the two esters) in Fig. 7. As was the case in the absence of NO, the yield of ethyl formate decreases with increasing O2 while the yield of ethyl acetate increases, consistent with a competition between 1-ethoxyethoxy decomposition reaction (3) and its reaction (6) with O_2 to generate ethyl acetate. Also, it is seen that the yield ratio does not reach unity at high temperature and low O₂ partial pressure, indicating the formation of a small (10-15%) yield of ethyl acetate under these conditions. Thus, there is clearly a source of ethyl acetate that does not result from the reaction (6) of 1-ethoxyethoxy with O_2 , an observation that is consistent with the observations of Cheema et al., and with their conclusion that H-atom elimination is a significant fate of 1-ethoxyethoxy in the presence of NO_x . Lastly,

it is apparent from Fig. 7 that the yield of ethyl formate does not tend to zero at low temperature and high O_2 partial pressure. This is a clear indication of a significant occurrence of activated decomposition of 1-ethoxyethoxy to produce ethyl formate, since the thermal decomposition should be essentially shut off under these conditions.

A more quantitative consideration of some of these points will now be presented. Consider a mechanism that allows for the formation and subsequent decomposition of activated 1-ethoxyethoxy *via* either CH₃ or H-atom elimination:

$$CH_{3}CH_{2}OCH(OO^{\bullet})CH_{3} + NO \rightarrow CH_{3}CH_{2}OCH(O^{\bullet})CH_{3} + NO_{2}$$
(2)

$$\rightarrow [CH_3CH_2OCH(O^{\bullet})CH_3]^* + NO_2 \qquad (2')$$

$$\begin{array}{l} CH_{3}CH_{2}OCH(OO^{\bullet})CH_{3} + NO \\ \rightarrow CH_{3}CH_{2}OCH(ONO_{2})CH_{3} \end{array} \tag{2b}$$

$$[CH_3CH_2OCH(O^{\bullet})CH_3]^* \rightarrow CH_3CH_2OCH(=O) + CH_3^{\bullet}$$
(3')

$$[CH_3CH_2OCH(O^{\bullet})CH_3]^* \rightarrow CH_3CH_2OC(=O)CH_3 + H$$

(4')

$$CH_{3}CH_{2}OCH(O^{\bullet})CH_{3} \rightarrow CH_{3}CH_{2}OCH(=O) + CH_{3}^{\bullet}$$
(3)

$$CH_{3}CH_{2}OCH(O^{\bullet})CH_{3} \rightarrow CH_{3}CH_{2}OC(=O)CH_{3} + H$$

$$(4)$$

$$\begin{array}{l} CH_{3}CH_{2}OCH(O^{\bullet})CH_{3} + O_{2} \\ \rightarrow CH_{3}CH_{2}OC(=O)CH_{3} + HO_{2} \end{array} \tag{6}$$

From this mechanism, the following expression can be derived to describe the product ratio:

$$Y(EF)/[Y(EF) + Y(EA)] = C + (1 - C - D)$$

× $k_3/([k_3 + k_4 + k_6[O_2])$ (B)

where Y(EF) and Y(EA) are the fractional molar yields of ethyl formate and ethyl acetate, respectively; *C* is the fraction of 1-ethoxyethoxy radicals decomposing *via* activated process (3'), *D* is the fraction of 1-ethoxyethoxy radicals decomposing *via* activated process (4'); and k_3 , k_4 , and k_6 are the rate coefficients for the corresponding thermal reactions (3), (4), and (6). Again, a minor occurrence of reaction (5) will have no influence on the results.

In an initial analysis, k_4 was assumed to be negligibly small, and expression (B) was fit to all the data in Fig. 7 with C, D, and the A-factor (A) and activation temperature (B) for the rate coefficient ratio $k_3/k_6 = A \exp(-B/T)$ as fit parameters. Best fit, shown as the solid lines in Fig. 7 and summarized in Table 2 and Fig. 4, was obtained with C = 0.47, D = 0.12, and $k_3/k_6 = 7.0 \times 10^{25} \exp(-3910/T)$ molecule cm⁻³. However, it was also found that equally good fits could be obtained by increasing the value of k_4 while simultaneously decreasing the value of D—*i.e.*, it is not possible to distinguish between thermal and activated H-atom loss from the 1-ethoxyethoxy radical. As an extreme case, a fit was conducted with the value of *D* fixed to zero; it was determined that good fits could be obtained with values for k_4 approximately 25–30% those for k_3 , independent of temperature. As discussed earlier, values for k_4 are unlikely to be this high and the fit obtained with $k_4 \approx 0$ is preferred.

It is clear from Fig. 4 that quantitative differences exist at low temperature between the k_3/k_6 ratios obtained with and without NO_x present. Because there is no obvious reason to prefer either dataset, it was thought that the best values for $k_3/$ k_6 could be obtained by merging the two datasets. In order not to excessively weight the NOx-free data, the 218 K data (obtained only with no NO_x present) were not included in the fit. The remainder of the dataset (data obtained at four temperatures, with and without NO_x) was then fit collectively, using six fit parameters: Two fit parameters were used to represent the intercept of the NO_x-free traces in Arrhenius form, two parameters were used to represent the ratio k_3/k_6 in Arrhenius form, and two parameters (C and D referred to above) were used to represent the activated decomposition of 1-ethoxyethoxy via processes (3') and (4') in the presence of NO_y. Best fit under this scenario was found with $k_3/k_6 = 6.9 \times$ $10^{24} \exp(-3130/T)$ molecule cm⁻³, and with C = 0.36 and D = 0.15. Comparisons of this fit (dashed lines) with the yield data are shown in Fig. 3 and 7, while the k_3/k_6 data are summarized in Table 2 and in Fig. 4. This fit (in which the two datasets are combined) provides a reasonable representation of the data, with 44 of the 48 vield ratio data points fit to within the uncertainty in their measured value. Largely via visual inspection of fits conducted on the entire dataset with the activation temperature systematically varied around its central value of 3130 K, uncertainties in the k_3/k_6 activation temperature are estimated at ± 600 K, with corresponding variations in the A-factor of a factor of 12. Lastly, uncertainty due to the possibility of a small contribution from reaction (9), ethyl formate production via initial attack at the CH₃ site, was considered. Recall from earlier in this section that this process contributes at most 10% to the chemistry. Extensive examination and re-fitting of the combined dataset, with ethyl formate vields appropriately adjusted, revealed that this reaction could introduce a high bias (10-45%, depending on the form of correction applied) in retrieved k_3/k_6 values, largely the result of potential effects on the data obtained in the absence of NO_{x} . Thus, to allow for this possibility, an asymmetric uncertainty in the activation temperature, 3130^{+600}_{-800} K, is adopted.

Despite these uncertainties, a number of quantitative conclusions can be drawn regarding the chemistry of the 1-ethoxyethoxy radical under atmospheric conditions:

(a) The rate coefficient ratio k_3/k_6 varies with temperature, decreasing from a value of about 2×10^{20} molecule cm⁻³ at 298 K to less than $\approx 6 \times 10^{18}$ molecule cm⁻³ at 218 K. The data imply a difference in activation energies between reaction (3) and reaction (6) of $6.2^{+1.2}/_{-1.6}$ kcal mol⁻¹.

(b) Under the assumption of the existence of a small ($\approx 0-1$ kcal mol⁻¹) barrier to reaction (6), typical for alkoxy radical reactions with O₂,¹¹ the barrier to methyl radical elimination from 1-ethoxyethoxy radical is then likely $6.7^{+1.7}/_{-2.1}$ kcal mol⁻¹. This is a very small activation barrier for an alkoxy radical C–C bond scission reaction, and reflects the strong

thermodynamic driving force to ester formation for the etherderived alkoxy radicals.

(c) Typically, rate coefficients for reaction of alkoxy radicals with O₂ are $\approx 10^{-14}$ cm³ molecule⁻¹ s^{-1,11} implying that the decomposition rate coefficient for 1-ethoxyethoxy is $k_3 \approx 2 \times 10^6$ at 298 K and $\approx 5 \times 10^4$ s⁻¹ at 220 K. Given that reaction (6) is likely more exothermic (and thus possibly faster) than typical alkoxy reactions with O₂, these values for k_3 likely represent lower limits.

(d) Activated decomposition of 1-ethoxyethoxy *via* process (3') is clearly occurring in the presence of NO_x, and accounts for about $\approx 30-50\%$ of the chemistry of the radicals generated from the reaction of the 1-ethoxyethylperoxy radical with NO.

(e) In keeping with the findings of Cheema *et al.*,⁷ there is clearly a source of ethyl acetate other than reaction (6) in the NO_x-based experiments—*i.e.*, a source that does not depend on O₂. This may arise from a small (10–15%) occurrence of activated decomposition of 1-ethoxyethoxy *via* (4'), or from a minor occurrence of reaction (4), or some combination of the two. On the basis of thermodynamics arguments, it seems more likely that activated decomposition provides the O₂-independent source of ethyl acetate.

(f) Ethyl formate will be the major product obtained from diethyl ether oxidation over the full range of conditions encountered in the troposphere, even in the coldest regions of the upper troposphere (*e.g.*, 12 km, 220 K, $[O_2] = 10^{18}$ molecule cm⁻³). This product will be formed from both thermal and activated decomposition of 1-ethoxyethoxy. However, there will also be a minor yield of ethyl acetate under all tropospheric conditions, as a result of activated H-atom elimination (or perhaps a minor occurrence of reaction (4)).

(g) The acetaldehyde yield appears to be rather small, less than 20% over the range of conditions studied. Given that two acetaldehydes result from each occurrence of reaction (5), it can be concluded $k_5 < 0.1 * k_3$. The upper limit for the acetaldehyde reported here is consistent with yields reported in previous studies at 298 K.^{5–7}

3. High temperature (335 K) experiments, with and without NO_x

A limited set of experiments was carried out at 335 K in both the presence and absence of NO_x over a range of O_2 partial pressures. In the presence of NO_x , the results obtained were consistent with expectations based on the lower temperature data. The total yield of the two ester products (78 ± 4%) was high and accounted for the majority of the oxidized DEE. Individual yields (ethyl formate, $67 \pm 5\%$; ethyl acetate, $11 \pm$ 3%) of the two ester products were found to be independent of O_2 , within experimental uncertainty, indicating that at elevated temperature the dissociation process (3) dominates the chemistry of thermalized 1-ethoxyethoxy radicals. At 335 K, reaction (6) with O_2 no longer contributes significantly and the only source of ethyl acetate in the system is *via* the (O_2 -independent) activated elimination of H-atom or from a minor occurrence of thermal reaction (4).

Results obtained in the absence of NO_x were, however, more intriguing. The yields of ethyl formate and ethyl acetate were both found to be independent of O_2 partial pressure, again indicating the lack of importance of reaction (6) at elevated temperatures and the predominance of reaction (3) in the 1-ethoxyethoxy chemistry. However, absolute yields of the two esters ($25 \pm 2\%$ for ethyl formate, and $19 \pm 2\%$ for ethyl acetate) were considerably reduced compared to those found at lower temperatures. Following subtraction of the absorption features due to DEE and the two ester products, a very complex residual absorption spectrum (peaks at 940, 1014, 1075, 1120, 1160, 1245, 1340, 1385, 1740, and 1780 cm⁻¹) remained. While some of these absorption features probably correspond to those observed in the absence of NO_x at lower temperatures, there were clearly new features present as well, in particular those at 940, 1014, 1075, 1250 and possibly 1775 cm⁻¹.

A single experiment was also carried out in 1 atm air at 355 K. Under these conditions, the ethyl formate yield was further reduced ($\leq 20\%$), while the ethyl acetate yield was not discernible due to spectral interferences. The absorption features at 940, 1014, 1075, and 1250 cm⁻¹ were even more prominent at this elevated temperature. The identity and origin of the species contributing to this residual spectrum are unknown at this time. The observation of a different mechanism in the absence of NO_x compared to its presence, however, is reminiscent of the work of Collins *et al.*,²¹ who recently published a study of diisopropyl ether (DIPE) oxidation at 298 K. These authors reported near-quantitative formation of isopropyl acetate and formaldehyde in the presence of NO_x, consistent with previous studies²² and consistent with the expected atmospheric peroxy and alkoxy radical chemistry:

 $\begin{array}{l} (CH_3)_2 C(OO^{\bullet})OCH(CH_3)_2 + NO \\ \rightarrow (CH_3)C(O^{\bullet})OCH(CH_3)_2 + NO_2 \end{array}$

 $(CH_3)_2C(O^{\bullet})OCH(CH_3)_2 \rightarrow CH_3C(=O)OCH(CH_3)_2 + CH_3$

However, in the absence of NO_x, yields of isopropyl acetate and formaldehyde were significantly reduced and acetone became a major oxidation product. Collins *et al.*²¹ suggested that, for thermalized (CH₃)₂C(O[•])OCH(CH₃)₂ radicals generated from peroxy radical self- and cross-reactions, a 1,4-H shift

 $(CH_3)_2C(O^{\bullet})OCH(CH_3)_2 \rightarrow CH_3C(OH)OC^{\bullet}(CH_3)_2$

was competing with the CH_3 -elimination reaction shown above, and was accounting for at least a portion of the observed acetone. It seems unlikely, however, that such an isomerization, occurring *via* a five-membered ring and likely occurring through a measurable barrier, would compete with what should be a very rapid C–C bond cleavage reaction.

It is tempting to consider the possibility that the change in mechanism observed in this work, and perhaps in the work of Collins *et al.* as well, originates from (thermal) unimolecular reactions of the peroxy radical, $CH_3CH_2OCH(OO^{\bullet})CH_3$ from DEE or $(CH_3)_2CHOC(OO^{\bullet})(CH_3)_2$ from DIPE. Note that the lifetime of the DEE-derived peroxy species in our chamber system increases from less than 1 ms in the presence of NO_x to hundreds of ms in its absence, thus potentially allowing for the occurrence of reasonably slow processes. Furthermore, as

there is no change in relative yields of the two ester products, there should be no significant change in the peroxy radical distribution and hence no change in the bimolecular chemistry associated with the peroxy species. Finally, the apparent strong temperature dependence to the change in mechanism is perhaps indicative of the participation of a unimolecular reaction.

A possible peroxy radical reaction to consider is H-atom transfer *via* a six-membered ring transition state:

$$CH_{3}CH_{2}OCH(OO^{\bullet})CH_{3} \rightarrow CH_{3}CH^{\bullet}OCH(OOH)CH_{3}$$
(14)

The analogous reaction, often designated $\text{RO}_2 \rightarrow \text{QOOH}$, is well known in alkylperoxy radical chemistry at elevated temperatures (see, for example, Taatjes²³ and references therein). Furthermore, the analogous rearrangement reaction has been shown to be of importance in the chemistry of dimethyl ether (DME) at high temperature and/or low pressure (*via* a chemically activated process),^{24–33} and it seems likely that isomerization will be energetically more favorable for the more substituted radicals derived from DEE or DIPE. A likely fate of the rearrangement product of reaction (14) is O₂ addition, leading to the formation of an array of multi-functional products.

To be of importance in this work, the thermal isomerization process (14) must occur with a barrier of less than about 17-18 kcal mol⁻¹. Studies of some related reactions—e.g., the 1,4-H atom shift in •O₂CH₂-CH=O,³⁴ and the 1,6-H atom shift in CH₃CH(OH)CH₂CH₂CH(OO[•])CH₃³⁵ or HOCH₂CH₂CH₂-CH(OO[•])CH₃³⁶—have generated barrier heights of roughly the required magnitude (14.5–19 kcal mol^{-1}). On the other hand, estimates of the barrier (18–24 kcal mol^{-1}) and/or rate for the 1,5-H shift in the DME-derived CH₃OCH₂OO• radical^{27,28,30,32} have generally shown this process to be too slow to be of importance near ambient temperature, and it is questionable as to whether the rearrangement process would be sufficiently enhanced in the DEE or DIPE cases to become important. Obviously, definitive conclusions regarding the observed change in mechanism cannot be made at this time. Nonetheless, this work and the study of Collins et al. suggest the occurrence of unknown peroxy radical chemistry at or near 298 K. Further theoretical and experimental studies of these substituted ether-derived peroxy species are clearly warranted, particularly given that their lifetimes may be greater than 1 s even in reasonably polluted (relatively high-NO_x) urban environments.

Summary

The Cl atom-initiated oxidation of diethyl ether has been studied under conditions relevant to the lower atmosphere, both in the presence and absence of NO_x. Ethyl formate and ethyl acetate are the major products observed under most conditions. The data show that decomposition *via* C–C bond cleavage, reaction (3), is the major fate of thermalized 1-ethoxyethoxy radical, CH₃CH₂OCH(O[•])CH₃, throughout the troposphere. The barrier to this decomposition process is about $6.7^{+1.7}/_{-2.1}$ kcal mol⁻¹. When formed from the

exothermic reaction of the corresponding peroxy radical with NO, decomposition of 1-ethoxyethoxy *via* an activated process (3') is clearly occurring, and accounts for about $\approx 30-50\%$ of the chemistry of the radicals generated in reaction (2). In addition, there are multiple sources of ethyl acetate in the system: reactions of CH₃CH₂OCH(OO[•])CH₃ radicals with themselves or with other peroxy radicals; reaction (6) of the 1-ethoxyethoxy radical with O₂; and, in the presence of NO_x, a small (10–15%) occurrence of activated decomposition of 1-ethoxyethoxy *via* H-atom elimination, reaction (4'). Finally, a change in mechanism (lower yields of ethyl formate and ethyl acetate) was noted at elevated temperature in the absence of NO_x, which might be the result of as-yet-undetermined chemistry of the peroxy radical, CH₃CH₂OCH(OO[•])CH₃.

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