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Gas Phase Reaction of Methyl n-Propyl Ether with OH, NO₃ and Cl: Kinetics and Mechanism

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ABSTRACT

Rate constants at room temperature (293 ± 2) K and atmospheric pressure for the reaction of methyl n-propyl ether (MnPE), CH₃OCH₂CH₂CH₃, with OH and NO₃ radicals, and Cl atom have been determined in a 100 L FEP-Teflon reaction chamber in conjunction with gas chromatography-flame ionization detector (GC-FID) as the detection technique. The obtained rate constants *k* (in units of cm³ molecule⁻¹ s⁻¹) are $(9.91 \pm 2.30) \times 10^{-12}$, $(1.67 \pm 0.32) \times 10^{-15}$, and $(2.52 \pm 0.14) \times 10^{-10}$ for reactions with OH, NO₃, and Cl, respectively. The products of these reactions were investigated by gas chromatography-mass spectrometry (GC-MS), and formation mechanisms are proposed for the observed reaction products. Atmospheric lifetimes of the studied ether, calculated from rate constants of the different reactions, reveal that the dominant loss process for MnPE is its reaction with OH, while in coastal areas and in the marine boundary layer, the MnPE loss by Cl reaction is also important.

INTRODUCTION

Oxygenated volatile organic compounds (OVOCs) belong to the large family of organic compounds present in the global atmosphere.¹ Atmospheric sources of OVOCs include direct emissions from a variety of anthropogenic and natural sources, and gas phase oxidation of organic compounds in the atmosphere.²⁻³ OVOCs may contribute to organic carbon in aerosols and participate in other atmospheric processes, which determine the oxidizing capacity of the atmosphere.^{1,4-5} In addition to their photochemical impact, many of these compounds are harmful to human health, especially in urban environments. Upon release into the troposphere, OVOCs can undergo either photolysis or photochemical oxidation by OH radical during daytime and by NO₃ radical during nighttime and Cl atom in the coastal regions.⁶ Reactions with OH, NO₃ or Cl are all important processes in the chemistry of natural and polluted atmosphere.⁷⁻⁸ However, their removal processes are well understood only for a few compounds. Although the chemistry of oxygenated organic compounds has been extensively explored over the past 50 years, much is yet to be discovered.³

Ethers form a class of OVOCs that have a wide range of practical applications, including fuel additives, alternative fuels and intermediates in chemical industries.⁹⁻¹³ The use and emissions of these compounds have led to increased interest into determining kinetics and mechanisms of their atmospheric degradation.¹⁴ The possible atmospheric significance of ethers is, thus, considered in terms of their reactions with oxidants,¹⁵ while reactions with O₃ are negligible.¹⁶ The kinetics of the symmetric short n-chain ethers, dimethyl ether (DME, CH₃OCH₃) and diethyl ether (DEE, CH₃CH₂OCH₂CH₃), have been the subject of numerous studies in the past. Rate constants of dimethyl ether oxidation by OH over the temperature range 299-427 K were measured using flash photolysis-resonance fluorescence (FP-RF) technique.¹⁷ The kinetics was described by an Arrhenius expression, $k(CH_3OCH_3) = 1.29 \times 10^{-11} e^{-(770 \pm 300)/RT} cm^3 molecule^{-1} s^{-1}$, with a rate constant at room temperature of $(3.50 \pm 0.35) \times 10^{-12} cm^3$ molecule⁻¹ s⁻¹. Using the FP-RF technique, reactions of dimethyl ether with Cl were studied and a rate constant of $(1.76 \pm 0.15) \times 10^{-10} cm^3$ molecule⁻¹ s⁻¹

 was obtained over the temperature range 200-500 K.¹⁸ An upper limit value of 4×10^{-16} cm³ molecule⁻¹ s⁻¹ for the rate constant of the reaction of NO₃ with CH₃OCH₃ was determined at 298 ± 2 K using flash photolysis technique.¹⁹ The relative rate method was used to measure the rate constants for the reaction of diethyl ether with OH, NO₃ and Cl, and values of $(5.6 \pm 1.1) \times 10^{-12}$, $(2.80 \pm 0.23) \times 10^{-15}$, and $(35.6 \pm 2.8) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ were reported, respectively.²⁰⁻²²

In contrast, only few studies on the kinetics and mechanism of reactions for asymmetric short n-chain ether have been reported. The kinetics and mechanism of methyl ethyl ether (MEE, CH₃OCH₂CH₃) were examined using FT-IR/relative-rate method, and rate constants of $(7.53 \pm 2.86) \times 10^{-12}$ and $(2.35 \pm 0.43) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ were obtained at 297 \pm 2 K for reactions with OH and Cl, respectively.²³ The rate constants for gas phase reactions between MEE with OH/Cl were determined using a relative rate technique and average values of $k_{\text{MEE+OH}} =$ $(6.60_{-2.62}^{+3.88}) \times 10^{-12}$ and $k_{\text{MEE+Cl}} = (34.9 \pm 6.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ were reported over the temperature range 274-345 K.²⁴ The measured rate constant of (7.81 ± 0.36 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ for MEE reaction with NO₃ was measured by means of a relative rate method at 298 K.²⁵ To our knowledge, there is only one theoretical study on the kinetics of the oxidation reaction of methyl n-propyl ether (MnPE, CH₃OCH₂CH₂CH₃) in the literature,²⁶ while no experimental study is available. However, MnPE was reported to be used as anesthetic and as organic solvent in some composite additives for gasoline systems,²⁷ and may be highly present in the atmosphere. High exposure to MnPE may lead to loss of appetite, headache, and dizziness followed by sleepiness and loss of consciousness.

We perform an experimental study on MnPE reactions with OH, NO₃ and Cl, at (293 \pm 2) K and atmospheric pressure, using the relative method with GC-FID and GC-MS as detection techniques. Reactions kinetics are determined and formation mechanisms of products are proposed. This study is essential to determine the lifetime and persistence of MnPE in the atmosphere, which can help to evaluate its impact on health and the environment.

EXPERIMENTAL AND METHODS

2.1. Kinetics Experiments

The experiments were performed in a 100 L FEP-Teflon reaction chamber (Figure 1) under room temperature (293 ± 2) K and atmospheric pressure. A Teflon made inlet and a similar outlet were used for the introduction of reactants and gas sampling, and Teflon tubes were used to connect the chamber and analytical instruments. The chamber was surrounded by a set of three UV fluorescent lamps (Philips TUV 36 W) with maximum intensity at 254 nm. Purified air was produced by a zero-air gas generator (Thermo Scientific, MODEL 111-D3R) and was used as bath gas. A drying tube was added after the zero-air gas generator to make sure the purified air had a low level relative humidity (<5%). The total volume of the gas in the chamber was measured with mass flow accumulator (Beijing Sevenstar, D80-8C/ZM). Liquid reactants were introduced into the chamber using graduated micro syringes and were evaporated into a stream of purified air as the chamber was filled. Prior to each experiment, the chamber was flushed with dried and purified air for at least three times.

Each reaction was measured with at least two reference standards. The reaction process was controlled by the exposure time in OH/Cl experiments and the adding mass of N₂O₅ in NO₃ experiments. Concentrations of MnPE and the reference compound were measured using a gas chromatograph equipped with a flame ionization detector (Agilent Technologies, GC-FID 7890B). The initial reactant concentrations are given in Table 1. The reaction gas in the chamber was extracted intermittently using a glass syringe and then introduced via a 0.5 mL Teflon loop mounted in a six-way valve onto a DB-624 capillary column (Agilent Technologies, 30 m length × 1.8 µm film thickness × 0.32 mm i.d.). To make sure that the peaks for each reference would not overlap with the reactant, different reference standards used different column temperatures. The chromatographic conditions used for the analysis were as follows: injector 523 K; split less injection; column flow 5 mL min⁻¹; FID heater 573 K.

2.2. Product Experiments

The product experiments followed similar procedure to that described above, except for the absence of reference compounds. Initial reactant concentrations are given in Table 1. In order to detect the products, two methods were used: thermal desorption and self-made cold trap.²⁸ Thermal desorption measured products by preconcentrating them on Tenax TA adsorption tubes (Markes International, 3.5-inch length and 0.25-inch O.D.). An air sampler (Beijing Municipal Institute of Labour Protection, QC-1S) was withdrawn from the chamber at a flow rate of 1.5 L min⁻¹ through Tenax TA adsorption tubes. The contents of the tubes were thermally desorbed at 473 K for 1 min in the stream of helium with a thermally desorption (Huashenpuxin, ATDS-3400A). The sample was rapidly heated to 523 K to inject the sample onto the HP-5ms capillary column (Agilent Technologies, 30 m length \times 0.50 µm film thickness \times 0.25 mm i.d.). The column was kept at 303 K for 14 min and then heated to 373 K at a heating rate of 5 K min⁻¹ and finally to 523 K at 10 K min⁻¹. The column was connected to a mass spectrometer (Agilent Technologies, 5977D MSD) operated in the total ion mode. Several samples were drawn through two Tenax TA adsorption tubes in series, which were both analyzed in the same way to check for breakthrough of the compounds in the adsorption tube.

A self-made cold trap using liquid nitrogen (77 K) was employed as the complementary method to concentrate the products. Gas samples were withdrawn through the cold trap until the chamber was evacuated. The trapped material was dissolved in 10 mL methanol and 1 μ L solution were injected into the GC-MS. Mass spectrometry detection was performed in electron impact (EI) mode with a detector temperature of 473 K. The conditions used for the analysis were as follows: injector 523 K; ion source 503 K; quadrupole 423 K; temperature program from 303 K to 403 K at a rate of 5 K min⁻¹ and finally to 523 K at 10 K min⁻¹.

2.3. Methods

Rate constants for the gas phase reactions of MnPE with OH, NO3 radicals and Cl

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atom were determined using the relative rate method, at (293 ± 2) K and atmospheric pressure. In the presence of oxidants (O_x), the substrate and the reference compounds decay through the following reactions:

$$O_X + MnPE \rightarrow products$$
 (R1)

$$O_X + Reference \rightarrow products$$
 (R2)

These decays are governed by the following rate equations:

$$d[MnPE]/dt = k_{MnPE} [MnPE] [O_X]$$
⁽¹⁾

$$d[Ref]/dt = k_{Ref} [Ref] [O_X]$$
⁽²⁾

where k_{MnPE} and k_{Ref} are rate constants of reactions (R1) and (R2), respectively. Assuming the reactant and the reference compound are only decayed by reactions (R1) and (R2), integration and rearrangement of equations (1) and (2) lead to the expression:

$$ln([MnPE]_0/[MnPE]_t) = k_{MnPE}/k_{Ref} ln([Ref]_0/[Ref]_t)$$
(3)

where, $[MnPE]_0$, $[Ref]_0$, $[MnPE]_t$ and $[Ref]_t$ are the concentrations of MnPE and reference compound at times t = 0 and t, respectively. Therefore, a plot of $ln([MnPE]_0/[MnPE]_t)$ versus $ln([Ref]_0/[Ref]_t)$ should be a straight line passing through the origin point with a slope of k_{MnPE}/k_{Ref} , and k_{MnPE} can then be obtained by multiplying the slope with the known value of k_{Ref} .

OH radicals were generated effectively by 254 nm photolysis of H_2O_2 .²⁹ Cl atoms were produced in site by 254 nm photolysis of SOCl₂ and CCl₃C(O)Cl. NO₃ radicals were generated from the thermal decomposition of dinitrogen pentoxide (N₂O₅).³⁰ N₂O₅ was prepared by reaction of fuming nitric acid with phosphorus oxide, and was intermittently introduced into the reaction chamber by a glass syringe.

The uncertainty on a rate constant measured with the relative rate method is determined with 2σ statistical error (Δ (expt)) from the regression analysis, consisting of random and systematic error, and the uncertainty of the reference rate constant (Δk (ref)), according to the equation:^{6,31}

$$\Delta k(\text{target}) = \sqrt{[\Delta k(ref)]^2 + [\Delta(expt)]^2}$$
(4)

One of the advantages of the relative rate measurements is that uncertainties in absolute concentrations of either reactant do not lead to an error in the measured rate constant values.³² The concentrations of the reactant and the reference compound were measured by using the same GC-FID system. The calibration curves for the VOC concentration versus their signals were linear. The precision of the measured signal contributes to the precision of the measured rate constants.³² The error in the values of $\Delta(\text{expt})$ are twice the standard deviation (2σ) in the least-squares fit of the measured losses to equation (3). In addition to the precision, the accuracy of the reference reactions. The experiments were performed under the temperature of (293 ± 2) K, therefore, the reference rate constants were chosen at a similar temperature. We combined the precision of our measured values with the quoted uncertainties in the rate coefficient for the reference reaction to estimate the overall accuracy of the measured rate constants using equation (4).

2.4. Chemicals

The chemicals were obtained commercially and were used without further purification: methyl n-propyl ether (C₄H₁₀O, >95.0%, TCI), thionyl chloride (SOCl₂, 99%, Adamas), trichloroacetyl chloride (CCl₃C(O)Cl, 99%, Adamas), cyclohexane (C₆H₁₂, \geq 99.9%, Aladdin), furan (C₄H₄O, \geq 99.0%, Aladdin), hydrogen peroxide solution (H₂O₂, 30wt% in H₂O, Aladdin), nitric acid fuming (HNO₃, \geq 98.0%, Sinopharm), phosphorus oxide (P₂O₅, \geq 98.0%, Tianjing Damao), tetrahydrofuran (C₄H₈O, 99%, TCI), acetaldehyde (CH₃CHO, 99.5%, Acros) and methanol (CH₃OH, \geq 99.9%, Aladdin). Propene (1%, N₂ as bath gas), He (\geq 99.999%), N₂ (\geq 99.999%), H₂ (\geq 99.999%) and synthetic compressed air were supplied by Jinan Deyang Special Gas Company, Shandong.

RESULTS AND DISCUSSION

3.1. Kinetics Studies

Several control experiments concerning wall loss, photolysis and dark reactions were

performed before the kinetics measurements to verify the assumption that reactants were solely removed by reactions with OH, NO₃ and Cl. Mixtures of MnPE and reference compounds were introduced into the chamber for the wall loss test in the absence of the radical precursors. Stable concentrations of the investigated compounds were monitored by GC-FID through at least ten measurements over the course of 5 h, and the integrated peak areas decreased by less than 3% of their initial values. Then, the mixtures were subjected to photolysis for twice the duration of each kinetics experiment without the radical precursors. Moreover, dark reactions were carried out between the radical precursors and mixtures of MnPE and reference compounds for the duration of each kinetics experiment. Based on the above described experiments, it was found that the loss occurred on the conversion of MnPE and reference compounds in the same time span of the radical reaction experiments.

3.1.1. Rate Constant of MnPE with OH

Cyclohexane, propene and furan were used as reference compounds because the rate constants of their reactions with OH were of same order of magnitude as the expected rate constant for the studied substrate. The rate constants for the reactions of OH with the reference compounds used were (in units of cm³ molecule⁻¹ s⁻¹): $(6.97 \pm 1.39) \times 10^{-12}$ for cyclohexane,³³ (2.51 ± 0.25) × 10⁻¹¹ for propene,³⁴ and (4.01 ± 0.30) × 10⁻¹¹ for furan.³⁵ Figure 2 shows examples of the kinetics data obtained from the experiments plotted according to equation (3) for MnPE, using cyclohexane, propene and furan as reference compounds. As expected for relative rate plots, straight lines with intercept at zero were obtained, indicating that the heterogeneous or secondary reactions were insignificant. For each reference compound, five experiments were carried out under different initial concentration ratios.

The obtained rate constants for MnPE reaction with OH are summarized in Table 2. The rate constants using different reference compounds are in reasonable agreement. The final rate constant for the reaction of OH with MnPE were concluded by averaging the rate constants obtained with each reference compound. The obtained rate constant for MnPE react with OH is $(9.91 \pm 2.30) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹. An equation was given to evaluate the overall rate constants *k* for ethers containing only primary and secondary C-H bonds,¹⁷

$$k = N_{\rm prim}k_{\rm prim} + N_{\rm sec}k_{\rm sec} \tag{5}$$

where N_{prim} , N_{sec} are the numbers of primary and secondary C-H bonds, respectively, and k_{prim} , k_{sec} are the rate constants for the reaction of the OH per primary or secondary C-H bond, respectively. Values of primary and secondary C-H bond are $k_{\text{prim}} = 6.0 \times 10^{-13}$ and $k_{\text{sec}} = 1.7 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 305 ± 2 K, respectively.¹⁷ The calculated rate constant, $k_{\text{MnPE}+\text{OH}} = 10.4 \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, agrees well with the experimental value.

A comparison of rate constants determined in this study with the literature data is shown in Table 3. There are a few reports about the rate constants for the reactions of OH with dimethyl ether (DME), methyl ethyl ether (MEE), diethyl ether (DEE) and methyl n-butyl ether (MnBE) by using absolute or relative rate methods at room temperature. For the studies of DME + OH, the largest rate constant of $(3.50 \pm 0.35) \times$ 10⁻¹² cm³ molecule⁻¹ s⁻¹ was determined by using absolute method and the smallest rate constant of $(2.32 \pm 0.23) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ was determined by using relative method.^{17,36} Discrepancy exists in the values obtained by using different methods. The accuracy of the results obtained in absolute rate methods might be limited by the concentration measurement.³⁷ In fact, a potential source of discrepancy could be an underestimation of the DME concentration in the experiment which would result in an overestimation of the rate coefficient. For the gas-phase atmospheric chemistry of MnPE with OH radicals, there was only one theoretical investigation carried out at 298.15 K using a variational transition state theory.²⁶ The obtained rate constant was 12.3×10^{-12} cm³ molecule⁻¹ s⁻¹, which is somewhat larger than our determination, but well within the stated uncertainly of $\pm 25\%$.³¹

Rate constants for OH reactions with DME, MEE, MnPE and MnBE are in the order: $k_{\text{DME + OH}} < k_{\text{MEE + OH}} < k_{\text{MnPE + OH}} < k_{\text{MnBE + OH}}$.^{23,36} Moreover, going from MEE to

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MnBE there is approximately a factor of 1.5 increase when adding a methyl group. The data are reasonably self-consistent and the results confirm the expected trend of the rate constants increasing as the molecules become larger and contain weaker C-H bonds.³⁸ Otherwise, reactions may occur mainly at the CH₂ groups, which explains the trend of increasing reactivity with increasing alkyl chain lengths.²³

Rate constants of DEE, MnPE and methyl i-propyl ether (MiPE) reactions with OH are in the order: $k_{\text{MiPE}+\text{OH}} < k_{\text{MnPE}+\text{OH}} < k_{\text{DEE}+\text{OH}}$.^{26,29} From the comparison, we can see that the symmetric ether, DEE, has largest rate constant and the asymmetric ether, MiPE, has smallest rate constant, which probably means that branched chains will decrease the reaction rate constant. The rate constant for OH reaction with ethyl t-butyl ether is nearly half of the rate constant of OH reaction with diethyl ether at room temperature.³⁹

Comparison of the rate constant for MnPE reaction with OH, $(9.91 \pm 2.30) \times 10^{-12}$ cm³ molecule⁻¹ s⁻¹, with the rate constant for butane reaction with OH, $(2.71 \pm 0.32) \times 10^{-12}$ cm³ molecule⁻¹ s^{-1,40} shows that the -OCH₃ group activates the C-H bond towards OH abstraction more than the -CH₃ group. The C-H bonds in ethers are significantly weaker than in corresponding alkanes. Owning to lower C-H bond dissociation energies for a carbon bound to an ether oxygen, as expected, reactivity toward OH is greatly enhanced.⁴¹ An analogous increase in the rate constant of OH reaction with methyl vinyl ether due to -CH₃ substitution by -OCH₃ have been observed.¹⁷ Such observations suggest that the -CH₂- groups in these molecules display essentially similar reactivity, which are approximately a factor of 3 greater than those observed in alkanes and not strongly dependent on their positions relative to the oxygen atom. The oxygen atom has an activating effect which is operative over long distances in aliphatic ether systems.⁴²

3.1.2. Rate Constant of MnPE with NO₃

The plots of rate constants of MnPE reaction with NO_3 using propene, tetrahydrofuran and acetaldehyde as reference compounds are shown in Figure 3, and numerical values of these rate constants have been determined to be (in units of cm³ molecule⁻¹ s⁻¹): $(9.45 \pm 0.47) \times 10^{-15}$ for propene, $(5.10 \pm 0.20) \times 10^{-15}$ for tetrahydrofuran and $(2.60 \pm 0.30) \times 10^{-15}$ for acetaldehyde.⁴³⁻⁴⁵ For each reference compound, the measurement was repeated three times under different initial concentration ratios of MnPE and reference compounds. The obtained rate constants for MnPE with NO₃ are summarized in Table 2. The rate constant obtained after averaging the values from different experiments was found to be $k_{\text{MnPE} + \text{NO3}} = (1.67 \pm 0.32) \times 10^{-15} \text{ cm}^3$ molecule⁻¹ s⁻¹.

In the literature, the rate constant for DME react with NO₃ was studied using a flash photolysis technique.¹⁹ The obtained value (3 × 10⁻¹⁵ cm³ molecule⁻¹ s⁻¹) is significantly larger than those values in other previous studies.^{21,25} The room temperature rate constant for the reaction of DEE with NO₃ has been reported with relative method. Comparing the rate constant with available data for NO₃ reaction with DME and MEE,^{21,25} we found that rate constants are in the order: $k_{DME + NO3} < k_{MEE + NO3} < k_{MnPE + NO3}$. The rate constant for NO₃ reaction with MEE is over two times for NO₃ reaction with DME. The rate constant of MnPE reaction with NO₃ is also over two times for NO₃ reaction with MEE. The rate constant of NO₃ reaction with butane (2.71 ± 0.32) × 10⁻¹².⁴⁰ The abstraction in ethers primary C-H and secondary C-H has low activation energy compared to the abstraction in alkanes. This lowering of the activation energy may be explained by the decrease in the C-H bond dissociation energy going from an ordinary carbon to a carbon bonded to an ether -O- group.²¹

3.1.3. Rate Constant of MnPE with Cl

SOCl₂ and CCl₃C(O)Cl were used as the chlorine source, and Cl atoms were generated by in situ photolysis of SOCl₂ or CCl₃C(O)Cl, while cyclohexane and propene were used as reference compounds. The rate constants of the reactions of Cl with the references have been reported to be (in units of cm³ molecule⁻¹ s⁻¹): (36.1 \pm 1.5) × 10⁻¹¹ for cyclohexane,²² (32.2 \pm 1.3) × 10⁻¹¹ for propene.⁴⁶ For each reference compound, the measurement was repeated five times under different initial concentration ratios of MnPE and reference compounds. The loss of MnPE is plotted

against the loss of the reference compounds in Figure 4.

The obtained rate constants of MnPE reaction with Cl are summarized in Table 2. Average rate constants when using SOCl₂ or CCl₃C(O)Cl are $(2.51 \pm 0.14) \times 10^{-10}$ and $(2.53 \pm 0.14) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, respectively. The difference in rate constants from the two precursors is very tiny. While averaging the values from different experiments, the rate constant was $k_{MnPE+Cl} = (2.52 \pm 0.14) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. There are some previous reports of the kinetics between DME and Cl atom.^{18,22,29,47.49} In addition, the kinetics of MEE with Cl has been carried out at (297 ± 2) K in the gas phase using FT-IR/relative-rate methods.²³ The difference between rate constants are close to collision controlled and it is possible that in this regime, substitution on the carbon chain induces very little changes in reaction rate constants.⁵⁰ Similar reason can explain why the rate constant for Cl reaction with MnPE differs very weakly from that of Cl reaction with butane, $(2.11 \pm 0.18) \times 10^{-10}$ cm³ molecule⁻¹ s^{-1.51}

Comparison of the reactivity of the three oxidants towards MnPE shows that the rate constant for the reaction with Cl is larger than those of reactions with OH (by two orders of magnitude) and NO₃ (by five orders of magnitude). It is important to mention that rate constants for Cl reactions are close to the gas kinetics limited value from gas collision theory, which means that the reaction probability is high regardless of collision site and that chemical structure plays a limited role in determining the reaction rate constant.^{6,50} Overall, the presence of oxygen atom in the ether linkage has been shown to exhibit an activating effect, which is operative up to the distance of 5 carbon atoms away from the linkage. This suggests reasons that ethers are more reactive than corresponding alkanes for OH, NO₃, and Cl attacks.²⁴

3.2. Reaction Mechanism

Seven main products were identified for the reaction of MnPE with OH radical as shown in Scheme 1: CH₃OCH₂CH₂CHO (14), CH₃OCH₂C(O)CH₃ (15), CH₃OOCCH₂CH₃ (16), CH₃CH₂CH₂OCHO (18), CH₃CHO (21), CH₃OCH₃CHO (24) and CH₃OCHO (26). From the proposed mechanism shown in Scheme 1, it is seen

that H-atom is abstracted by the OH radical from the two primary and two secondary C-H bonds in the molecule. The observed products, upon which the proposed reactions are based, are highlighted in boxes in Scheme 1. Some analogous products, such as CH₃C(O)OCH₃, CH₃CH₂OCHO, CH₃OCHO and CH₃CHO, were detected in the CH₃CH₂OCH₃ reaction with Cl experiment using FT-IR.²³

Path 1 shows the reaction occurring after H-atom abstraction by OH radical from the primary C-H bond on the propyl side of MnPE. The initial carbon-centred radical is formed by H-atom abstraction, followed by O_2 addition to form the peroxy radical (6). The peroxy radical (6) undergoes self-reaction and cross reaction with other peroxy radicals to mainly produce the alkoxy radical (10). The intermediate alkoxy radical (10) further reacts with O_2 to yield the corresponding 3-methoxypropanal (14). In addition, the alkoxy radical has been shown to undergo direct hydrogen atom elimination which would yield the same end products.⁴⁷ An additional decomposition pathway leads to the formation of formaldehyde (19) and the alkoxy radical (20).

Path 2 shows the proposed reactions following H-atom abstraction from the CH₂ group which is far away from the methoxy group. The intermediate alkoxy radical (11) decomposes mainly via the rupture of C-C bond to form methoxyacetaldehyde (24) and methyl radical (27). The alkoxy radical (11) reacts with oxygen, leading to 1-methoxyacetone (15). Alternatively, the alkoxy radical (11) may decompose via breakage of the C-C bond, yielding acetaldehyde (21) and alkoxy radical (22). Besides, the 1,5-hydrogen shift (H-shift) is possible for the H abstraction at β -CH₂ group. As a further possibly important reaction, alkoxy radical (11) is expected to undergo isomerization via 1,5-H shift by abstracting an H atom from the primary C-H in the methyl group of the ether. The resulting organic radical (29) leads most likely to the formation of alkoxy radical (30) and formaldehyde (19) via breakage of the C-C bond. Similar to the alkoxy radical [CH₃CH₂OCH₂(O^{*})] derived from formate,²³ alkoxy radical (11) is proposed to undergo reaction with oxygen leading to the organic formate (31).

Path 3 shows the proposed reactions following H-atom abstraction from the CH₂

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group which is close to the methoxy group. The alkoxy radical (12) decomposes through rupture of C-C bond to form the products, methyl formate (26) and ethyl group (25). By analogy with forming 1-methoxyacetone (15), the alkoxy radical (12) reacts with oxygen to generate methyl propanoate (16). The alternative decomposition reaction would lead to propyl aldehyde (17) and methoxy radical (28).

In path 4, the OH attack occurs on the methyl group of the methoxy side chain. The resulting alkoxy radical (13) may react with oxygen to form propyl formate (18), or decompose to form formaldehyde (19) and alkoxy radical (23). By analogy with alkoxy radicals (10) derived from methyl ether $[CH_3OCH_2(O^{\bullet})]$, the alkoxy radical (13) is proposed to mainly undergo reaction with oxygen or C-H bond fission, leading to alkoxy radical (23) and formaldehyde (19).

Overall the proposed mechanisms reasonably give observed products. Furthermore, the proposed reaction mechanisms for the formation of the major products are based entirely on the established gas phase reactions. Carbonyl compounds such as aldehydes, ketones, and esters are first generation products from MnPE reactions. The branching ratios for the different paths contributing to the overall reaction of MnPE with OH were investigated with variational transition state theory.²⁶ The overall rate constants percentage for paths 1, 2, 3 and 4 were reported to contribute for 0.73%, 10.65%, 57.98% and 30.64% to the MnPE + OH reaction at 298.15 K, respectively.²⁶ From branching ratios, we can see that the presence of the O atom in the vicinity of the H abstraction site increases its reactivity toward OH radicals. This influence was found to be even larger than that of the nature of the carbon site (primary, secondary, tertiary).²⁶

Methyl propanoate (16) and propyl formate (18) were detected for the reaction of MnPE with Cl, and product (16) was also identified in the MnPE + NO₃ reaction. The three types of C-H groups in the MnPE molecule would lead to the formation of three structurally different types of oxy radicals: type I [CH₂(O^{*})OCH₂CH₂CH₃ or CH₃OCH(O^{*})CH₂CH₃] has an alkoxy substituent in the α -position relative to the radical center; type II [CH₃OCH₂CH(O^{*})CH₃], derived from the propyl side, has an

alkoxy substituent in the β -position relative to the radical center; whereas type III [CH₃OCH₂CH₂CH₂(O[•])] has an alkoxy substituent in the γ -position relative to the radical center. In general, the OH-initiated oxidation of ethers is believed to generate mainly oxy radicals of type I.⁵² Analogous to the CH₃OCH₂CH₃ and CH₃CH₂OCH₂CH₃, C-H bonds at the α sites are weaker than the C-H bonds at the β sites.²⁵ For the same reason, we believe that by attacking MnPE on C-H at the α -position, reactions with Cl or NO₃ are the dominant initial processes. These reactions lead to the formation of the major product in the process, methyl propanoate (16). Scheme S1 in the supporting information shows a general mechanism proposed for the reaction of MnPE with the three atmospheric oxidants: OH, NO₃ radicals and Cl atoms.

3.3. Atmospheric Implications

Ethers are released into the atmosphere from biogenic and anthropogenic sources and are degraded in the troposphere almost exclusively via their reactions with OH, NO₃ radicals and Cl atoms. Accurate kinetic data and mechanistic information, at atmospheric temperatures, for the reactivity of OH, NO₃, and Cl toward VOCs are needed in order to determine the lifetimes of these compounds in the troposphere and assess their impact on urban air pollution. In particular, tropospheric lifetimes with respect to reactions with oxidants are key parameters in calculating the ozone formation potential of VOCs.⁵³

Atmospheric lifetimes (τ) of the studied MnPE based on its reactions with atmospheric oxidants, are calculated using equation (6) below,

$$\tau_X = \frac{1}{k_X [X]} \tag{6}$$

where [X] is the concentration of the oxidant and k_x is the reaction rate constant. The calculated atmospheric lifetimes are presented in Table 4. Oxidants concentrations considered in this study were as follow: 12 h average day time global concentration of OH of 1×10^6 molecules cm⁻³ (global weighted-average concentration), 24 h average of Cl atom concentration of 5×10^3 molecules cm⁻³ or the concentration in the marine

 boundary layer of 1×10^5 molecules cm⁻³ and 12 h average night time concentration of NO₃ of 5×10^8 molecules cm⁻³.⁵⁴⁻⁵⁸

These results indicate that in the atmosphere, the degradation of MnPE is mainly due to reaction with OH, since the calculated lifetime is 28 h. The lifetime of MnPE due to reaction with NO₃ is ten times higher than that due to reaction with OH. The reaction with NO₃ during night time may be negligible for MnPE at ambient conditions. The MnPE lifetime due to reaction with Cl was estimated to be 220 h. However, it should be noted that in the coastal areas and in the marine boundary layer, the concentration of Cl atoms can be as high as 1×10^5 atoms cm⁻³,⁵⁵ making the H-atom abstraction by Cl atom an additional and possibly significant degradation pathway of MnPE. In the marine boundary layer, this process could compete with the reaction with OH.

CONCLUSION

In the light of our results, the kinetic and mechanistic data for reactions of methyl n-propyl ether (MnPE) with OH, NO₃ and Cl are presented. Using the relative rate method, the rate constants for MnPE reaction with OH, NO₃ and Cl were determined to be $(9.91 \pm 2.30) \times 10^{-12}$, $(1.67 \pm 0.32) \times 10^{-15}$ and $(2.52 \pm 0.14) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, respectively. The obtained data show that MnPE reaction with Cl is faster than those with OH and NO₃. Reactions with the three oxidants mainly lead to the formation of some esters and aldehydes, which are pollutants involved in photochemical smog and likely to affect health. Formation mechanisms are proposed for the observed reaction products. Atmospheric lifetimes of MnPE were calculated with respect to reactions with OH/NO₃/Cl using corresponding rate constants at room temperature. The obtained lifetimes indicate that reaction with Cl becomes a significant removal process only in the marine boundary layer.

ASSOCIATED CONTENT

Supporting Information

General mechanism proposed for the reaction of MnPE with the three atmospheric oxidants: OH, NO₃ and Cl.

ACKNOWLEDGMENTS

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REFERENCES

1. Singh, H.; Chen, Y.; Staudt, A.; Jacob, D.; Blake, D.; Heikes, B.; Snow, J., Evidence from the Pacific troposphere for large global sources of oxygenated organic compounds. *Nature* **2001**, *410* (6832), 1078-1081.

2. Mellouki, A.; Le Bras, G.; Sidebottom, H., Kinetics and mechanisms of the oxidation of oxygenated organic compounds in the gas phase. *Chem. Rev.* **2003**, *103* (12), 5077-5096.

3. Mellouki, A.; Wallington, T. J.; Chen, J., Atmospheric chemistry of oxygenated volatile organic compounds: Impacts on air quality and climate. *Chem. Rev.* **2015**, *115* (10), 3984-4014.

4. Lewis, A. C.; Carslaw, N.; Marriott, P. J.; Kinghorn, R. M.; Morrison, P.; Lee, A. L.; Bartle, K. D.; Pilling, M. J., A larger pool of ozone-forming carbon compounds in urban atmospheres. *Nature* **2000**, *405* (6788), 778-781.

5. Kalberer, M.; Paulsen, D.; Sax, M.; Steinbacher, M.; Dommen, J.; Prevot, A.; Fisseha, R.; Weingartner, E.; Frankevich, V.; Zenobi, R., Identification of polymers as major components of atmospheric organic aerosols. *Science* **2004**, *303* (5664), 1659-1662.

6. Taccone, R. A.; Moreno, A.; Colmenar, I.; Salgado, S.; Martín, M. P.; Cabañas, B., Kinetic study of the OH, NO₃ radicals and Cl atom initiated atmospheric photo-oxidation of iso-propenyl methyl ether. *Atmos. Environ.* **2016**, *127*, 80-89.

7. Finlayson-Pitts, B. J.; Pitts, J. N., Tropospheric air pollution: ozone, airborne toxics, polycyclic aromatic hydrocarbons, and particles. *Science* **1997**, *276* (5315), 1045-1051.

8. Atkinson, R., Atmospheric chemistry of VOCs and NO_x. *Atmos. Environ.* **2000**, *34* (12), 2063-2101.

9. Japar, S.; Wallington, T.; Richert, J.; Ball, J., The atmospheric chemistry of oxygenated fuel additives: t-butyl alcohol, dimethyl ether, and methyl t-butyl ether. *Int. J. Chem. Kinet.* **1990**, *22* (12), 1257-1269.

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10. Langer, S.; Ljungströem, E., Reaction of the nitrate radical with some potential automotive fuel additives. A kinetic and mechanistic study. *J. Phys. Chem.* **1994**, *98* (23), 5906-5912.

11. Worrell, E.; Phylipsen, D.; Einstein, D.; Martin, N., Energy use and energy intensity of the US chemical industry. *Lawrence Berkeley National Laboratory* **2000**.

12. Semelsberger, T. A.; Borup, R. L.; Greene, H. L., Dimethyl ether (DME) as an alternative fuel. *J. Power Sources* **2006**, *156* (2), 497-511.

13. Arcoumanis, C.; Bae, C.; Crookes, R.; Kinoshita, E., The potential of di-methyl ether (DME) as an alternative fuel for compression-ignition engines: A review. *Fuel* **2008**, *87* (7), 1014-1030.

14. Nielsen, O. J.; Sehested, J.; Langer, S.; Ljungström, E.; Wängberg, I., UV absorption spectra and kinetics for alkyl and alkyl peroxy radicals originating from di-tert-butyl ether. *Chem. Phys. Lett.* **1995**, *238* (4-6), 359-364.

15. Mcloughlin, P.; Kane, R.; Shanahan, I., A relative rate study of the reaction of chlorine atoms (Cl) and hydroxyl radicals (OH) with a series of ethers. *Int. J. Chem. Kinet.* **1993**, *25* (3), 137-149.

16. Atkinson, R.; Carter, W. P., Kinetics and mechanisms of the gas-phase reactions of ozone with organic compounds under atmospheric conditions. *Chem. Rev.* **1984**, *84* (5), 437-470.

17. Perry, R.; Atkinson, R.; Pitts Jr, J., Rate constants for the reaction of OH radicals with dimethyl ether and vinyl methyl ether over the temperature range 299-427 K. *J. Chem. Phys.* **1977**, *67* (2), 611-614.

18. Michaela, J.; Nava, D.; Payne, W.; Stiefb, L., Rate constants for the reaction of atomic chlorine with methanol and dimethyl ether from 200 to 500 K. *J. Chem. Phys.* **1979**, *70* (8), 3652-3656.

19. Wallington, T.; Atkinson, R.; Winer, A.; Pitts Jr, J., Absolute rate constants for the gas-phase reactions of the NO₃ radical with CH₃SH, CH₃SCH₃, CH₃SSCH₃, H₂S, SO₂, and CH₃OCH₃ over the temperature range 280 - 350 K. *J. Phys. Chem.* **1986**, *90* (21), 5393-5396.

20. Lloyd, A. C.; Darnall, K. R.; Winer, A. M.; Pitts, J. N., Relative rate constants for the reactions of OH radicals with isopropyl alcohol, diethyl and di-n-propyl ether at 305 ± 2 K. *Chem. Phys. Lett.* **1976**, *42* (2), 205-209.

21. Langer, S.; Ljungström, E., Rates of reaction between the nitrate radical and some aliphatic ethers. *Int. J. Chem. Kinet.* **1994,** *26* (3), 367-380.

22. Wallington, T. J.; Skewes, L. M.; Siegl, W. O.; Wu, C. H.; Japar, S. M., Gas phase reaction of Cl atoms with a series of oxygenated organic species at 295 K. *Int. J. Chem. Kinet.* **1988**, *20* (11), 867-875.

23. Andersen, M. P.; Svendsen, S. B.; Østerstrøm, F. F.; Nielsen, O. J., Atmospheric chemistry of CH₃CH₂OCH₃: kinetics and mechanism of reactions with Cl atoms and OH radicals. *Int. J. Chem. Kinet.* **2017**, *49* (1), 10-20.

24. Starkey, D. P.; Holbrook, K. A.; Oldershaw, G. A.; Walker, R. W., Kinetics of the reactions of hydroxyl radicals (OH) and of chlorine atoms (Cl) with methylethylether over the temperature range 274-345 K. *Int. J. Chem. Kinet.* **1997**, *29* (3), 231-236.

25. Chen, L.; Uchimaru, T.; Kutsuna, S.; Tokuhashi, K.; Sekiya, A.; Okamoto, H.,

Kinetics of gas-phase reactions of CH₃OCH₂CF₃, CH₃OCH₃, CH₃OCH₂CH₃, CH₃OCH₂CH₃ and CHF₂CF₂OCH₂CF₃ with NO₃ radicals at 298 K. *Int. J. Chem. Kinet.* **2009**, *41* (7), 490-497.

26. Zavala-Oseguera, C.; Alvarez-Idaboy, J. R.; Merino, G.; Galano, A., OH radical gas phase reactions with aliphatic ethers: a variational transition State Theory Study. *J. Phys. Chem. A* **2009**, *113* (50), 13913-13920.

27. Hartman, D. E., *Neuropsychological toxicology: Identification and assessment of human neurotoxic syndromes.* Springer Science & Business Media: 1995.

28. Stemmler, K.; Mengon, W.; Kinnison, D. J.; Kerr, J. A., OH radical-initiated oxidation of 2-butoxyethanol under laboratory conditions related to the troposphere: product studies and proposed mechanism. *Environ. Sci. Technol.* **1997**, *31* (5), 1496-1504.

29. Nelson, L.; Rattigan, O.; Neavyn, R.; Sidebottom, H.; Treacy, J.; Nielsen, O. J., Absolute and relative rate constants for the reactions of hydroxyl radicals and chlorine atoms with a series of aliphatic alcohols and ethers at 298 K. *Int. J. Chem. Kinet.* **1990**, *22* (11), 1111-1126.

30. Atkinson, R.; Plum, C. N.; Carter, W. P.; Winer, A. M.; Pitts Jr, J. N., Rate constants for the gas-phase reactions of nitrate radicals with a series of organics in air at 298 ± 1 K. *J. Phys. Chem.* **1984**, *88* (6), 1210-1215.

31. Kramp, F.; Paulson, S. E., On the uncertainties in the rate coefficients for OH reactions with hydrocarbons, and the rate coefficients of the 1, 3, 5-trimethylbenzene and m-xylene reactions with OH radicals in the gas phase. *J. Phys. Chem. A* **1998**, *102* (16), 2685-2690.

32. Zhou, L.; Ravishankara, A. R.; Brown, S. S.; Idir, M.; Zarzana, K. J.; Daele, V.; Mellouki, A., Kinetics of the reactions of NO₃ radical with methacrylate esters. *J. Phys. Chem. A* **2017**, *121* (23), 4464-4474.

33. Atkinson, R., Kinetics of the gas-phase reactions of OH radicals with alkanes and cycloalkanes. *Atmos. Chem. Phys.* **2003**, *3* (6), 2233-2307.

34. Atkinson, R.; Pitts Jr, J., Rate constants for the reaction of OH radicals with propylene and the butenes over the temperature range 297-425 K. J. Chem. Phys. **1975**, *63* (8), 3591-3595.

35. Atkinson, R.; Aschmann, S. M.; Carter, W. P., Kinetics of the reactions of O_3 and OH radicals with furan and thiophene at 298 ± 2 K. *Int. J. Chem. Kinet.* **1983**, *15* (1), 51-61.

36. Wallington, T. J.; Andino, J. M.; Skewes, L. M.; Siegl, W. O.; Japar, S. M., Kinetics of the reaction of OH radicals with a series of ethers under simulated atmospheric conditions at 295 K. *Int. J. Chem. Kinet.* **1989**, *21* (11), 993-1001.

37. Messaadia, L.; El Dib, G.; Lendar, M.; Cazaunau, M.; Roth, E.; Ferhati, A.; Mellouki, A.; Chakir, A., Gas-phase rate coefficients for the reaction of 3-hydroxy-2-butanone and 4-hydroxy-2-butanone with OH and Cl. *Atmos. Environ.* **2013**, *77*, 951-958.

38. Bennett, P. J.; Kerr, J. A., Kinetics of the reactions of hydroxyl radicals with aliphatic ethers studied under simulated atmospheric conditions. *J. Atmos. Chem.* **1989**, $\delta(1)$, 87-94.

 39. Bennett, P. J.; Kerr, J. A., Kinetics of the reactions of hydroxyl radicals with aliphatic ethers studied under simulated atmospheric conditions: temperature dependences of the rate coefficients. *J. Atmos. Chem.* **1990**, *10* (1), 27-38. 40. Atkinson, R.; Aschmann, S. M., Rate constants for the reaction of OH radicals with a series of alkenes and dialkenes at 295 ± 1 K. *Int. J. Chem. Kinet.* **1984**, *16* (10),

1175-1186. 41. Tully, F. P.; Droege, A. T., Kinetics of the reactions of the hydroxyl radical with dimethyl ether and diethyl ether. *Int. J. Chem. Kinet.* **1987**, *19* (3), 251-259.

42. Wallington, T. J.; Liu, R.; Dagaut, P.; Kurylo, M. J., The gas phase reactions of hydroxyl radicals with a series of aliphatic ethers over the temperature range 240-440 K. *Int. J. Chem. Kinet.* **1988**, *20* (1), 41-49.

43. Atkinson, R., Kinetics and mechanisms of the gas-phase reactions of the NO₃ radical with organic compounds. *J. Phys. Chem. Ref. Data* **1991**, *20* (3), 459-507.

44. D'Anna, B.; Andresen, O.; Gefen, Z.; Nielsen, C. J., Kinetic study of OH and NO₃ radical reactions with 14 aliphatic aldehydes. *Phys. Chem. Chem. Phys.* **2001**, *3* (15), 3057-3063.

45. Cabañas, B.; Baeza, M. T.; Salgado, S.; Martín, P.; Taccone, R.; Martínez, E., Oxidation of heterocycles in the atmosphere: kinetic study of their reactions with NO₃ radical. *J. Phys. Chem. A* **2004**, *108* (49), 10818-10823.

46. Wallington, T. J.; Skewes, L. M.; Siegl, W. O., Kinetics of the gas phase reaction of chlorine atoms with a series of alkenes, alkynes and aromatic species at 295 K. *J. Photochem. Photobiol. A* **1988**, *45* (2), 167-175.

47. Jenkin, M. E.; Hayman, G. D.; Wallington, T. J.; Hurley, M. D.; Ball, J. C.; Nielsen, O. J.; Ellermann, T., Kinetic and mechanistic study of the self-reaction of methoxymethylperoxy radicals at room temperature. *J. Phys. Chem.* **1993**, *97* (45), 11712-11723.

48. Notario, A.; Mellouki, A.; Le Bras, G., Rate constants for the gas-phase reactions of Cl atoms with a series of ethers. *Int. J. Chem. Kinet.* **2000**, *32* (2), 105-110.

49. Giri, B. R.; Roscoe, J. M., Kinetics of the reactions of Cl atoms with several ethers. J. Phys. Chem. A 2010, 114 (32), 8369-8375.

50. Blanco, M. B.; Barnes, I.; Teruel, M. A., FTIR gas-phase kinetic study of the reactions of Cl atoms with (CH₃)₂CCHC(O)H and CH₃CHCHC(O)OCH₃. *Chem. Phys. Lett.* **2010**, *488* (4), 135-139.

51. Beichert, P.; Wingen, L.; Lee, J.; Vogt, R.; Ezell, M. J.; Ragains, M.; Neavyn, R.; Finlayson-Pitts, B. J., Rate constants for the reactions of chlorine atoms with some simple alkanes at 298 K: measurement of a self-consistent set using both absolute and relative rate methods. *J. Phys. Chem.* **1995**, *99* (35), 13156-13162.

52. Kwok, E. S.; Atkinson, R., Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: An update. *Atmos. Environ.* **1995**, *29* (14), 1685-1695.

53. Mellouki, A.; Teton, S.; Le Bras, G., Kinetics of OH radical reactions with a series of ethers. *Int. J. Chem. Kinet.* **1995**, *27* (8), 791-805.

54. Bloss, W. J.; Evans, M. J.; Lee, J. D.; Sommariva, R.; Heard, D. E.; Pilling, M. J., The oxidative capacity of the troposphere: Coupling of field measurements of OH and

a global chemistry transport model. Faraday Discuss. 2005, 130, 425-436.

 55. Spicer, C.; Chapman, E.; Finlayson-Pitts, B.; Plastridge, R.; Hubbe, J.; Fast, J.; Berkowitz, C., Unexpectedly high concentrations of molecular chlorine in coastal air. *Nature* **1998**, *394* (6691), 353-356.

56. Pszenny, A.; Keene, W.; Jacob, D. J.; Fan, S.; Maben, J.; Zetwo, M.; Springer-Young, M.; Galloway, J., Evidence of inorganic chlorine gases other than hydrogen chloride in marine surface air. *Geophys. Res. Lett.* **1993**, *20* (8), 699–702.

57. Wingenter, O. W.; Kubo, M. K.; Blake, N. J.; Smith, T. W.; Blake, D. R.; Rowland, F. S., Hydrocarbon and halocarbon measurements as photochemical and dynamical indicators of atmospheric hydroxyl, atomic chlorine, and vertical mixing obtained during Lagrangian flights. *J. Geophys. Res.* **1996**, *101*, 4331-4340.

58. Shu, Y.; Atkinson, R., Atmospheric lifetimes and fates of a series of sesquiterpenes. J. Geophys. Res. **1995**, 100 (D4), 7275-7281.

59. Arif, M.; Dellinger, B.; Taylor, P. H., Rate coefficients of hydroxyl radical reaction with dimethyl ether and methyl tert-butyl ether over an extended temperature range. *J. Phys. Chem. A* **1997**, *101* (13), 2436-2441.

60. DeMore, W.; Bayes, K., Rate constants for the reactions of hydroxyl radical with several alkanes, cycloalkanes, and dimethyl ether. *J. Phys. Chem. A* **1999**, *103* (15), 2649-2654.

61. Bonard, A.; Daële, V.; Delfau, J.-L.; Vovelle, C., Kinetics of OH radical reactions with methane in the temperature range 295-660 K and with dimethyl ether and methyl-tert-butyl ether in the temperature range 295-618 K. *J. Phys. Chem. A* **2002**, *106* (17), 4384-4389.

62. Bänsch, C.; Kiecherer, J.; Szöri, M.; Olzmann, M., Reaction of dimethyl ether with hydroxyl radicals: kinetic isotope effect and prereactive complex formation. *J. Phys. Chem. A* **2013**, *117* (35), 8343-8351.

63. Semadeni, M.; Stocker, D. W.; Kerr, J. A., Further studies of the temperature dependence of the rate coefficients for the reactions of OH with a series of ethers under simulated atmospheric conditions. *J. Atmos. Chem.* **1993**, *16* (1), 79-93.

64. Chew, A. A.; Atkinson, R.; Aschmann, S. M., Kinetics of the gas-phase reactions of NO₃ radicals with a series of alcohols, glycol ethers, ethers and chloroalkenes. *J. Chem. Soc., Faraday Trans.*, **1998**, *94* (8), 1083-1089.

65. Wallington, T. J.; Dagaut, P.; Liu, R.; Kurylo, M. J., Rate constants for the gas phase reactions of OH with C5 through C7 aliphatic alcohols and ethers: Predicted and experimental values. *Int. J. Chem. Kinet.* **1988**, *20* (7), 541-547.

TABLES AND FIGURES

Table	1.	Reactant	concentrations,	for	the	kinetic	experiments	and	the	product	evaluation	for	the
reaction	s of	OH, NO ₃	and Cl with Mr	PE a	at 29	93 ± 2 K	and atmosph	neric	pres	sure			

Reactants	Concentration				
	ppm	10^{15} molecules cm ⁻³			
Kinetics experiments					
MnPE	57.8-115.6	1.4-2.8			
H_2O_2	377.6	9.3			
N_2O_5	283.0-424.5	7.0-10.4			
SOCl ₂	256.9	6.3			
CCl ₃ C(O)Cl	142.8	3.5			
Cyclohexane	58.1-116.2	1.4-2.9			
Propylene	62.5-147.6	1.5-3.6			
Furan	80.9-161.8	2.0-4.0			
Tetrahydrofuran	76.4-152.8	1.9-3.8			
Acetaldehyde	97.2-194.5	2.4-4.8			
Products experiments					
MnPE	57.8	1.4			
H_2O_2	377.6	8.3			
N_2O_5	283.0-424.5	7.0-10.4			
SOCl ₂	256.9	6.3			

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Oxidant	Reference	k _{MnPE}	$k_{MnPE\ (average)}$		
		cm ³ molecule ⁻¹ s ⁻¹	cm ³ molecule ⁻¹ s ⁻¹		
OH	Cyclohexane	$(10.03 \pm 1.39) \times 10^{-12}$	$(9.91 \pm 2.30) \times 10^{-12}$		
	Propene	$(9.82 \pm 2.50) \times 10^{-12}$			
	Furan	$(9.88 \pm 3.00) \times 10^{-12}$			
Cl	Cyclohexane ^a	$(2.51 \pm 0.15) \times 10^{-10}$	$(2.52 \pm 0.14) \times 10^{-10}$		
	Propene ^a	$(2.51 \pm 0.13) \times 10^{-10}$			
	Cyclohexane ^b	$(2.55 \pm 0.15) \times 10^{-10}$			
	Propene ^b	$(2.50 \pm 0.13) \times 10^{-10}$			
NO ₃	Propene	$(2.08 \pm 0.47) \times 10^{-15}$	$(1.67 \pm 0.32) \times 10^{-15}$		
	Tetrahydrofuran	$(1.33 \pm 0.20) \times 10^{-15}$			
	Acetaldehyde	$(1.61 \pm 0.30) \times 10^{-15}$			

Table 2. Summary of rate constants for the reaction of MnPE with OH, NO₃, and Cl at 293 ± 2 K and atmospheric pressure of air

^a SOCl₂ as Cl atoms precursor.

^b CCl₃C(O)Cl as Cl atoms precursor.

Table 3. Rate constant for the reaction of OH, NO₃ radicals and Cl atom with selected short chain ethers

Compound	$k_{OH}^{a} \times 10^{-12}$	Т, К	Method ^b	$k_{Cl}^{a} \times 10^{-10}$	Т, К	Method ^b	k_{NO3} ^a ×10 ⁻¹⁵	Т, К	Method ^b
CH ₃ OCH ₃	3.50 ± 0.35 ¹⁷	298.9	FP-RF	1.80 ± 0.09^{-18}	300	FP-RF	3 19	298 ± 2	FP
Dimethyl ether (DME)	$2.95 \pm 0.12 \ ^{41}$	295	LP-LIF	$2.05\pm 0.08\ ^{22}$	295 ± 2	RR	0.26 ± 0.11^{21}	295	RR
	2.49 ± 0.22 ⁴²	296	FP-RF						
	2.32 ± 0.23^{-36}	295	RR	1.51 ± 0.08^{29}	298 ± 2	RR	0.11 ± 0.01^{-25}	298	RR
	2.35 ± 0.24^{29}	298 ± 2	PR	$1.90\pm 0.10^{\;47}$	298	RR			
	3.19 ± 0.70^{29}	298 ± 2	PRR	$1.30\pm 0.20\ ^{48}$	298 ± 2	LP-RF			
	2.82 ± 0.21^{-53}	298	PLP-LIF	1.58 ± 0.14^{49}	299.8	RR			
	2.95 ± 0.21^{-59}	295	LP-LIF						
	2.86 60	298	RR						
	2.67 ± 0.7 ⁶¹	298	PLP-LIF						
	2.58 ± 0.75 ⁶²	298	PLP-LIF						
CH ₃ OCH ₂ CH ₃	6.87 _{-2.40} +3.72 24	301	RR	3.18 ± 0.34^{24}	303	RR	0.78 ± 0.036 ²⁵	298	RR
Methyl ethyl ether (MEE)	7.53 ± 2.86^{23}	297 ± 2	FT-IR/RR	$2.35\pm 0.43\ ^{23}$	297 ± 2	RR			
CH ₃ CH ₂ OCH ₂ CH ₃	9.4 ± 1.9^{20}	305 ± 2	RR	3.56 ± 0.28^{22}	295 ± 2	RR	2.80 ± 0.23^{21}	295	RR
Diethyl ether (DEE)	13.4 ± 0.6^{41}	295	LP-LIF						
	13.6 ± 0.9^{42}	296	FP-RF	$2.54 \pm 0.17^{\ 29}$	298 ± 2	RR	3.1 ± 1.0^{-64}	298 ± 2	RR
	12.0 ± 1.1^{-38}	294 ± 2	RR	2.58 ± 0.44 ¹⁵	300 ± 3	RR	$2.80 \pm 0.10^{\ 25}$	298	RR
	10.0 ± 0.18^{39}	294	RR	$2.50\pm 0.30^{\;48}$	298 ± 2	LP-RF			
	11.3 ± 0.10^{29}	298 ± 2	PR						
	12.8 ± 0.6^{29}	298 ± 2	PRR						
	12.4 ± 1.15^{63}	298	RR						
	13.6 ± 1.1^{53}	298	PLP-LIF						
CH ₃ OCH ₂ CH ₂ CH ₃	9.91 ± 2.30 °	295 ± 2	RR	2.52 ± 0.14 °	295 ± 2	RR	1.67 ± 0.32 °	295 ± 2	RR
Methyl n-propyl ether (MnPE)	12.3 ²⁶	298.15	Theory						

CH ₃ OCH(CH ₃) ₂ Methyl i-propyl ether (MiPE)	7.09 ²⁶	298.15	Theory			
CH ₃ OCH ₂ CH ₂ CH ₂ CH ₃	16.4 ± 0.6^{65}	298	FP-RF			
Methyl n-butyl ether (MnBE)	12.9 ± 0.3^{-36}	295	RR			
	15.0 ± 1.2^{63}	298	RR			

^a Rate constant in units (cm³ molecule⁻¹ s⁻¹).

^b FP-RF, flash-photolysis-resonance fluorescence; LP-LIF, laser photolysis-laser induced fluorescence; PR, Pulse-radiolysis; PRR, photolytic relative rate; PLP-LIF, pulse-laser photolysis-laser induced fluorescence; LP-RF, laser photolysis-resonance fluorescence.

^c This work.

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Table 4. Atmospheric lifetimes for the reaction of MnPE with OH, NO ₃ radicals	s and Cl atom
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Compound	$\tau_{OH}^{a}(h)$	$\tau_{Cl}^{b}(h)$	$\tau_{Cl}^{c}(h)$	$\tau_{NO3}^{d}(h)$	
MnPE	28.03	220.46	11.02	332.67	
3 4 5 1			106 1 1	-3	

 a 12 h average day time global concentration of OH of 1 \times 10 6 molecules cm $^3.$

 b 24 h average of Cl atom concentration of 5×10^{3} molecules cm $^{-3}.$

^c Cl atom concentration in the marine boundary layer of 1×10^5 molecules cm⁻³.

 d 12 h average night time concentration of NO3 of 5×10^8 molecules cm $^{-3}.$



Figure 1. Schematic diagram of the 100 L chamber used to study the reaction of OH, NO₃ and Cl with MnPE along with the analytical methods used to detect reactants and products.



Figure 2. Relative rate plots for OH reactions with MnPE, using cyclohexane (\blacksquare), propene (\bullet) and furan (\blacktriangle) as reference compounds.



Figure 3. Relative rate plots for NO₃ reactions with MnPE, using propene (\blacksquare), tetrahydrofuran (\bullet) and acetaldehyde (\blacktriangle) as reference compounds.



Figure 4. Relative rate plots for Cl reactions with MnPE, using cyclohexane (triangle) and propene (circle) as reference compounds. Solid symbols represent $CCl_3C(O)Cl$ as the Cl source and empty symbols represent $SOCl_2$ as the Cl source.



Scheme 1. Proposed reaction pathways for the reaction of MnPE with OH radicals.

TOC Graphic

