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Kinetic Study of the Gas-Phase Reactions of OH and NO_3 Radicals and O_3 with Selected Vinyl Ethers

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Kinetic studies on the gas-phase reactions of OH and NO_3 radicals and ozone with ethyl vinyl ether (EVE), propyl vinyl ether (PVE) and butyl vinyl ether (BVE) have been performed in a 405 L borosilicate glass chamber at 298 ± 3 K in synthetic air using in situ FTIR spectroscopy to monitor the reactants. Using a relative kinetic method rate coefficients (in units of cm^3 $molecule^{-1}$ s^{-1}) of $(7.79 \pm 1.71) \times 10^{-11}$, $(9.73 \pm 1.94) \times 10^{-11}$ and $(1.13 \pm 0.31) \times 10^{-10}$ have been obtained for the reaction of OH with EVE, PVE and BVE, respectively, $(1.40 \pm 0.35) \times 10^{-12}$, $(1.85 \pm 0.53) \times 10^{-12}$ and $(2.10 \pm 0.54) \times 10^{-12}$ for the reaction of NO_3 with EVE, PVE and BVE, respectively, and $(2.06 \pm 0.42) \times 10^{-16}$, $(2.34 \pm 0.48) \times 10^{-16}$ and $(2.59 \pm 0.52) \times 10^{-16}$ for the ozonolysis of EVE, PVE and BVE, respectively. Tropospheric lifetimes of EVE, PVE and BVE with respect to the reactions with reactive tropospheric species (OH, NO_3 and O_3) have been estimated for typical OH and NO_3 radical and ozone concentrations.

Introduction

A wide range of oxygenated volatile organic compounds (OVOCs) have been detected in the atmosphere.[1−6] They are emitted directly into the troposphere from biogenic and anthropogenic sources and are also formed in situ in the atmosphere as a result of the photooxidation of all hydrocarbons. There has been increased interest lately in the atmospheric chemistry of organic oxygenates mainly with respect to the roles that they play in indoor pollution and in secondary organic aerosol formation and also the potential toxicity of some of the oxygenates.[7−10] However, in comparison to the expansive kinetic and mechanistic database available on the gas-phase reactions of alkanes, alkenes and aromatic hydrocarbons, information on the gas-phase reactions of oxygenated organic compounds is currently limited to a relatively small range of compounds.[10−18]

Vinyl ethers ($ROCH{=}CH_2$) are widely applied in industry as oxygenated solvents, additives and in different types of coatings[19,20] and are released to the atmosphere entirely from anthropogenic sources. Due to the presence of the alkene moiety in vinyl ethers it is to be expected that they will show moderate to high reactivity toward the major atmospheric oxidants, i.e., OH and NO_3 radicals and ozone and, under certain circumstances, possibly Cl atoms. To date only limited kinetic and product data are available in the literature on the gas-phase reactions of a few vinyl ethers with OH[9,21−25] and NO_3 radicals[9,22,25] and O_3.[7,22,25−27] To better assess the potential environmental impacts of vinyl ethers, we report here kinetic studies on the OH and NO_3 radical and ozone initiated oxidation of ethyl vinyl ether (EVE; $C_2H_5{-}O{-}CH{=}CH_2$), propyl vinyl ether (PVE; $n\text{-}C_3H_7{-}O{-}CH{=}CH_2$) and butyl vinyl ether (BVE; $n\text{-}C_4H_9{-}O{-}CH{=}CH_2$).

Experimental Setup and Procedures

All the experiments were performed in a 405 L glass chamber at 298 ± 3 K in synthetic air. A detailed description of the reactor can be found elsewhere[28] and only a brief description is given here. The chamber is composed of a cylindrical borosilicate glass vessel (1.5 m long and 60 cm inner diameter) closed at both ends by Teflon-coated aluminum flanges. It can be evacuated by a pumping system consisting of a turbomolecular pump backed by a double stage rotary fore pump to 10^{-3} Torr. A magnetically coupled Teflon mixing fan is mounted inside the chamber to ensure homogeneous mixing of the reactants. Two types of lamps were used in the experiments: 18 fluorescent lamps (Philips TLA 40 W/05; $\lambda_{max} = 360$ nm) spaced evenly around the outside of the reactor and 3 low-pressure mercury vapor lamps (Philips TUV40W; $\lambda_{max} = 254$ nm) placed inside a quartz glass tube mounted centrally inside the main reactor vessel and supported by the end flanges. The lamps are wired in parallel and can be switched individually, which allows a variation of the light intensity, and thus also the photolysis frequency/radical production rate, within the chamber.

A White-type mirror system mounted internally in the chamber and coupled to a FTIR spectrometer Nicolet Magna 550 enables in situ monitoring of the reactants in the infrared range 4000−700 cm^{-1}. The White system was operated with the total optical absorption path set to 50.4 m and infrared spectra were recorded with a spectral resolution of 1 cm^{-1}.

A relative kinetic technique was used to determine the rate coefficients for the reactions of OH and NO_3 radicals and O_3 with EVE, PVE and BVE. In this technique the disappearance of the vinyl ether (VE) due to reaction with the reactive species

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(OH, NO_3 or O_3) is measured relative to that of a reference compound, whose rate coefficient with the reactive species is reliably known, e.g., for OH:

$$\mathrm{VE + OH \rightarrow products} \qquad k_1 \tag{1}$$

$$\mathrm{reference + OH \rightarrow products} \qquad k_2 \tag{2}$$

Additionally, vinyl ethers and the reference hydrocarbons could be lost to the reactor walls or photolyze. Test experiments showed that wall loss and photolysis were negligible for all the reference compounds employed. However, when vinyl ethers were admitted into the chamber, in addition to wall loss, dark decays of the compounds were observed, accompanied by the formation of new bands in the IR spectrum that could be assigned to acetaldehyde (CH_3CHO) and an alcohol. For example, the dark loss of PVE resulted in the formation of CH_3CHO and propanol (C_3H_7OH). This process was not enhanced in the presence of light showing that photolytic losses of vinyl ethers are negligible. The enhanced loss of the vinyl ethers at the walls is attributed to acid catalyzed hydrolysis, e.g.,

$$\mathrm{CH_2{=}CH{-}O{-}C_3H_7 + H^+ \rightarrow CH_3{-}CH^+{-}O{-}C_3H_7}$$

$$\mathrm{CH_3CH^+{-}O{-}C_3H_7 + H_2O \rightarrow CH_3CHO + C_3H_7OH + H^+}$$

The combined dark decay and wall loss was found to obey first-order kinetics and can be represented by

$$\mathrm{VE\ (dark\ decay\ and\ wall\ loss) \rightarrow products} \qquad k_3 \tag{3}$$

The following equation has been used to evaluate the kinetic data:

$$\ln\left\{\frac{[\mathrm{VE}]_{t_0}}{[\mathrm{VE}]_t}\right\} - k_3(t-t_0) = \frac{k_1}{k_2}\ln\left\{\frac{[\mathrm{reference}]_{t_0}}{[\mathrm{reference}]t}\right\} \tag{I}$$

where $[\mathrm{VE}]_{t_0}$ and $[\mathrm{reference}]_{t_0}$ are the concentrations of the vinyl ether and reference compound, respectively, at time t_0; $[\mathrm{VE}]_t$ and $[\mathrm{reference}]_t$ are the corresponding concentrations at time t; k_1 and k_2 are the rate coefficients for the reaction of VE and reference with OH radicals, respectively; k_3 is the dark loss rate of VE. Plots of $\ln([\mathrm{VE}]_{t_0}/[\mathrm{VE}]_t) - k_3(t-t_0)$ versus $\ln([\mathrm{reference}]_{t_0}/[\mathrm{reference}]_t)$ should give straight lines with slopes of k_1/k_2. The rate constant k_1 can be derived from the known rate coefficient k_2. Because the dark loss of vinyl ether is a first-order reaction, its rate k_3 can be derived from the slope of plots of $\ln([\mathrm{VE}]_{t_0}/[\mathrm{VE}]_t)$ versus time before reaction 1 is initiated. Frequent checks were made to verify that the dark losses of the vinyl ethers did not change during the course of the reaction by measuring their rates in the pre- and postreaction periods. The dark loss accounted for between 5 and 10% of the overall decay of the vinyl ethers.

The rate coefficients for the reactions of NO_3 radicals and ozone with the vinyl ethers were determined in a manner analogous to that described above for the reactions of OH with the vinyl ethers.

OH Radical Reaction. Kinetic experiments for the reactions of OH radicals with selected vinyl ethers were performed at 750 ± 10 Torr total pressure of synthetic air using isobutene and isoprene as reference compounds. Photolysis of methyl nitrite (CH_3ONO) was used for the production of OH radicals,

$$\mathrm{CH_3ONO} + h\nu \rightarrow \mathrm{CH_3O + NO}$$

$$\mathrm{CH_3O + O_2 \rightarrow CH_2O + HO_2}$$

$$\mathrm{HO_2 + NO \rightarrow NO_2 + HO}$$

The initial concentrations of the vinyl ethers and reference compounds were approximately 5.0 ppm (1 ppm = 2.46×10^{13} molecule cm^{-3} at 298 K) and 4.9−5.5 ppm, respectively; those of CH_3ONO and NO were 1.5−4.0 ppm and 9.8−19.8 ppm, respectively. NO was added to the reaction mixture to suppress the formation of O_3 and NO_3 radicals. The reactants were monitored in the infrared at the following absorption frequencies (in cm^{-1}): EVE at 3129.4 and 1612.7; PVE at 965, 1211.2 and 3129; BVE at 3128.9 and 1614; isobutene at 890; isoprene at 893.4 and 905.9.

NO_3 Radical and Ozone Reactions. All the experiments on the reactions of NO_3 radicals and O_3 with EVE, PVE and BVE were performed at 740 ± 10 Torr total pressure of synthetic air. NO_3 radicals were produced by the thermal dissociation of N_2O_5 prepared in solid form according to a literature method:[29]

$$\mathrm{N_2O_5 + M \rightarrow NO_3 + NO_2 + M}$$

Multiple additions of N_2O_5 were made to a mixture of the vinyl ether and reference compound. N_2O_5 was added to the chamber by passing air over the surface of solid N_2O_5, which was placed in a cold trap at −50 °C. Similarly, for the investigations on the ozonolysis of the vinyl ethers, ozone was added stepwise to mixtures containing the vinyl ether, cyclohexene and cyclohexane, where cyclohexene was used as the reference hydrocarbon and cyclohexane was present in excess to scavenge any OH radicals produced in the reaction of ozone with the vinyl ether. An electrical discharge in a flow of pure oxygen was used to generate ozone.

The initial concentrations of the reactants for the NO_3 experiments were approximately vinyl ethers 5.0 ppm, isoprene 4.9−5.5 ppm, and 2,3-dimethyl-1,3-butadiene 4.8 ppm. For the ozone experiments they were vinyl ethers 2.7−5.5 ppm, cyclohexene 3.8−7.3 ppm, O_3 1.0−1.8 ppm, and cyclohexane 290 ppm. The reactants were monitored at the following infrared absorption frequencies (in cm^{-1}): EVE at 3129.4 and 1612.7; PVE at 965, 1211.2 and 3129; BVE at 3128.9 and 1614; isoprene at 893.4 and 905.9; 2,3-dimethyl-1,3-butadiene at 895; cyclohexene at 1139.7.

Results and Discussion

OH Radical Reaction. Rate coefficients for the reactions of OH with EVE, PVE and BVE have been measured using isobutene and isoprene as the reference compounds. Examples of the kinetic data plotted according to eq I for the three vinyl ethers investigated are shown in Figure 1. Good linear relationships were found for all three vinyl ethers with both reference compounds. The rate coefficient ratios k_1/k_2, obtained from a minimum of three experiments at 298 K are listed in Table 1. The rate coefficients, k_1, determined for the reactions of OH with EVE, PVE and BVE, which were put on an absolute basis using values of k_2(isobutene, 298 K) = 5.14×10^{-11} and k_2(isoprene, 298 K) = 1.01×10^{-10} cm^3 $molecule^{-1}$ s^{-1},[30] are listed in Table 1. The quoted errors are a combination of the least squares standard deviation 2σ plus an additional 20% to cover uncertainties in the values of the rate coefficients for the references. As can be seen in Table 1, there is excellent agreement between the values obtained using the two different reference compounds. We, therefore, prefer to quote rate coefficients for the reactions of OH with the vinyl ethers that

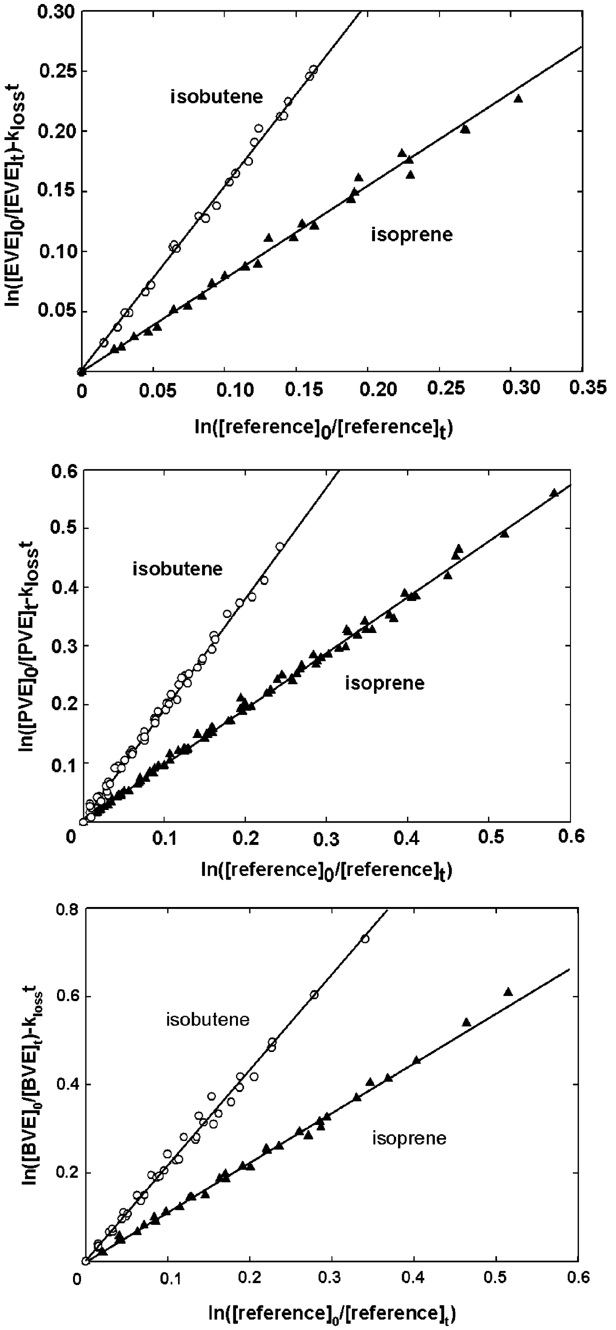

Figure 1. Plots of the kinetic data according to eq I for the gas-phase reaction of OH radicals with (i) ethyl vinyl ether (EVE), (ii) propyl vinyl ether (PVE) and (iii) butyl vinyl ether (BVE). The plots have been labeled with the reference compound used.

TABLE 1: Measured Rate Coefficient Ratios, k_1/k_2, and Rate Coefficients (cm^3 molecule^{-1} s^{-1}) for the Reactions of OH with EVE, PVE and BVE Obtained in the Present Work at 298 K Using the Relative Kinetic Technique

vinyl ether	reference	k_1/k_2	$10^{11}k_1$	av $10^{11}k_1$
EVE,	isobutene	1.54 ± 0.03	7.91 ± 1.60	7.79 ± 1.71
$C_2H_5OCH{=}CH_2$	isoprene	0.76 ± 0.03	7.66 ± 1.58	
PVE,	isobutene	1.89 ± 0.03	9.71 ± 1.96	9.73 ± 1.94
$C_3H_7OCH{=}CH_2$	isoprene	0.95 ± 0.02	9.75 ± 1.00	
BVE,	isobutene	2.13 ± 0.06	10.9 ± 2.2	11.3 ± 3.1
n-$C_4H_9OCH{=}CH_2$	isoprene	1.14 ± 0.04	11.5 ± 2.4	

TABLE 2: Comparison of the Rate Coefficients (cm^3 molecule^{-1} s^{-1}) Measured in the Present Work at 298 K for the Reactions of OH with EVE, PVE and BVE with Values Reported in the Literature Data for These and Other Vinyl Ethers at the Same Temperature

vinyl ether	$10^{11}k$	technique [ref]
MVE,	3.35 ± 0.34	FP−RF [21][a]
$CH_3OCH{=}CH_2$	4.5 ± 0.7	relative rate [24]
	6.4	SAR-estimation [22]
EVE,	6.8 ± 0.7	PLP−LIF [23,24][b]
$C_2H_5OCH{=}CH_2$	7.3 ± 0.9	relative rate [23,24]
	7.79 ± 1.71	relative rate [tw][c]
PVE,	10 ± 1	PLP−LIF [24]
$C_3H_7OCH{=}CH_2$	11 ± 1	relative rate [24]
	9.73 ± 1.94	relative rate [tw][c]
BVE,	10 ± 1	PLP−LIF [24][b]
n-$C_4H_9OCH{=}CH_2$	11 ± 1	relative rate [24]
	11.3 ± 3.1	relative rate [tw][c]
IBVE,	11 ± 1	PLP−LIF [24][b]
i-$C_4H_9OCH{=}CH_2$	11 ± 1	relative rate [24]
TBVE,	11 ± 1	PLP−LIF [24][b]
t-$C_4H_9OCH{=}CH_2$	11 ± 1	relative rate [24]

[a] Flash photolysis−resonance fluorescence (FP−RF), Arrhenius expressions for the temperature range 299−427 K are reported. [b] Pulsed laser photolysis−laser induced fluorescence (PLP−LIF), Arrhenius expressions for the temperature range 230−373 K are reported. [c] This work.

are averages of the determinations using both reference compounds. Averaging the values of the rate coefficients and taking errors that encompass the extremes of both determinations for each reaction give rate coefficients at 298K of k_1(OH+EVE) = (7.79 ± 1.71) × 10^{-11}, k_1(OH+PVE) = (9.73 ± 1.94) × 10^{-11} and k_1(OH+BVE) = (11.3 ± 3.1) × 10^{-11} cm^3 molecule^{-1} s^{-1}. These values are listed in Table 2 where they are compared with the available literature kinetic data on alkyl vinyl ethers.

The rate coefficients measured for the reaction of OH with EVE, PVE and BVE in this study are in excellent agreement with the values reported by Mellouki et al.[23,24] which were obtained using pulsed laser photolysis−laser induced fluorescence (PLP−LIF) and also a relative kinetic technique. There is generally good agreement between the various determinations of the rate coefficients for the reactions of OH with vinyl ethers. The only exception is the value of 6.4 × 10^{-11} cm^3 molecule^{-1} s^{-1} estimated by Grosjean and Williams[22] from structure−activity relationships (SAR) and linear free-energy relationships (LFER) for the reaction of OH with methyl vinyl ether (MVE), which is substantially higher than the two experimentally determined values.[21,24]

In Table 1 it can be seen that there is an increase in the rate coefficients for the reactions of OH with the vinyl ethers on progressing from MVE through EVE, PVE to BVE, thereafter the rate coefficients for isobutyl vinyl ether (IBVE) and *tert*-butyl vinyl ether (TBVE) are indistinguishable from that of BVE. The rate coefficients for the reaction of OH with alkyl vinyl ethers are higher than those of OH with simple ethers (ROR, R = alkyl group) and significantly higher than those of OH with the corresponding alkenes.[9,24] As discussed by Mellouki et al.,[9,24] the kinetic evidence supports that the alkoxy groups, −OR, in vinyl ethers activate the double bond toward electrophilic addition by OH more than alkyl groups, −R. Whereas the rate coefficients for the reaction of OH with alkenes do not seem to be influenced very much by the nature of the R group ($k_{(OH+alkene)} \approx 3 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} for R = CH_3 to C_4H_9) those of OH with vinyl ethers increase from approximately 4 × 10^{-11} for R = CH_3O to 1.1 × 10^{-10} cm^3 molecule^{-1} s^{-1} for R = $CH_3CH_2CH_2CH_2O$. However, based on our measurements and the values reported by Mellouki[24] given in Table 1, it would appear that for alkoxy chains longer than C_4 the electron donating influence of the RO group on the double bond toward electrophilic addition of OH radicals has reached a limiting value.

The effect of the RO entity on the reactivity of the double toward OH addition can also be compared with that of other oxygenated entities, i.e., a vinyl carbonyl ($CH_2{=}CH{-}CO{-}R$), a vinyl ester grouping ($CH_2{=}CH{-}OC(O)R$), and an alkyl acrylate grouping ($CH_2{=}CH{-}C(O)OR$), where R is an H atom or alkyl group. There is not presently a large database for the type of oxygenated compound listed, but from the data that are available,[11,12,30−33] the OH radical reactions with the vinyl ethers are somewhat faster than the reactions with the corresponding $CH_2{=}CH{-}CO{-}R$, $CH_2{=}CH{-}OC(O)R$ and $CH_2{=}CH{-}C(O)OR$ compounds. A deactivating effect on the rate of electrophilic OH addition to the double bond from the $-COR$, $-OC(O)R$ and $-C(O)OR$ constellations is to be expected because of the negative inductive effect introduced by the carbonyl functionality. In the case of vinyl aldehydes the decrease in the reactivity of the double bond is offset to some extend by H-atom abstraction of the aldehydic hydrogen. The meager kinetic dataset presently available on the oxygenates does not warrant a more detailed comparison at this time.

NO_3 Radical Reaction. The rate coefficients for the reactions of NO_3 with EVE, PVE and BVE were measured relative to isoprene and 2,3-dimethyl-1,3-butadiene. Examples of the kinetic data, obtained from measurements on the vinyl ethers relative to both reference compounds, are plotted according to eq I in Figure 2. For all three vinyl ethers good linear relationships were obtained using both reference compounds. The rate coefficient ratios, k_1/k_2, obtained from these plots are listed in Table 3. Using these ratios in combination with $k_2(\text{isoprene}) = 6.78 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} and k_2(2,3-dimethyl-1,3-butadiene) $= 2.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} [31] leads to the rate constants k_1 for the reaction of NO_3 with EVE, PVE and BVE which are also listed in Table 3. The errors are again the standard 2σ deviation plus an additional 20% to cover uncertainties in the values of the rate coefficients for the reference compounds. The rate coefficients obtained for each vinyl ether using the two reference compounds are in reasonable agreement.

Since the last data evaluation on NO_3 kinetics known to us,[31] Kind et al. [34] have reported a rate constant of 1.4×10^{-12} cm^3 molecule^{-1} s^{-1} for the reaction of NO_3 with 2,3-dimethyl-1,3-butadiene, which is one of the reference compounds used in this study. The value of Kind et al.[34] reported is much lower than previous determinations. Using this value gives rate coefficients (in cm^3 molecule^{-1} s^{-1}) of $(0.97 \pm 0.20) \times 10^{-12}$, $(1.32 \pm 0.28) \times 10^{-12}$ and $(1.47 \pm 0.30) \times 10^{-12}$ for the reactions of NO_3 with EVE, PVE and BVE, respectively. These values are not in as good agreement with those obtained with isoprene when the currently recommended value of 2.1×10^{-12} cm^3 molecule^{-1} s^{-1} [33] is used as the rate coefficient for NO_3 + 2,3-dimethyl-1,3-butadiene.

To resolve this reference problem, we tried to substitute 2,3-dimethyl-1,3-butadiene with another reference compound; however, for all of the potentially suitable substitute compounds selected, we unfortunately experienced interferences in the FTIR analysis. Therefore, because Kind et al. could offer no explanation for the discrepancy, we prefer to use the value of 2.1×10^{-12} cm^3 molecule^{-1} s^{-1} as the rate coefficient for the reaction of NO_3 with 2,3-dimethyl-1,3-butadiene in the calculation of the rate coefficients for NO_3 with the vinyl ethers studied in this work. Thus, we cite here final rate coefficients at 298 K (in units of cm^3 molecule^{-1} s^{-1}) of $k_1(NO_3{+}EVE) = (1.40 \pm 0.35) \times 10^{-12}$, $k_1(NO_3{+}PVE) = (1.85 \pm 0.53) \times 10^{-12}$, and $k_1(NO_3{+}BVE) = (2.10 \pm 0.54) \times 10^{-12}$, which are averages of the values obtained using the two reference compounds with error limits which encompass the extremes of both determinations.

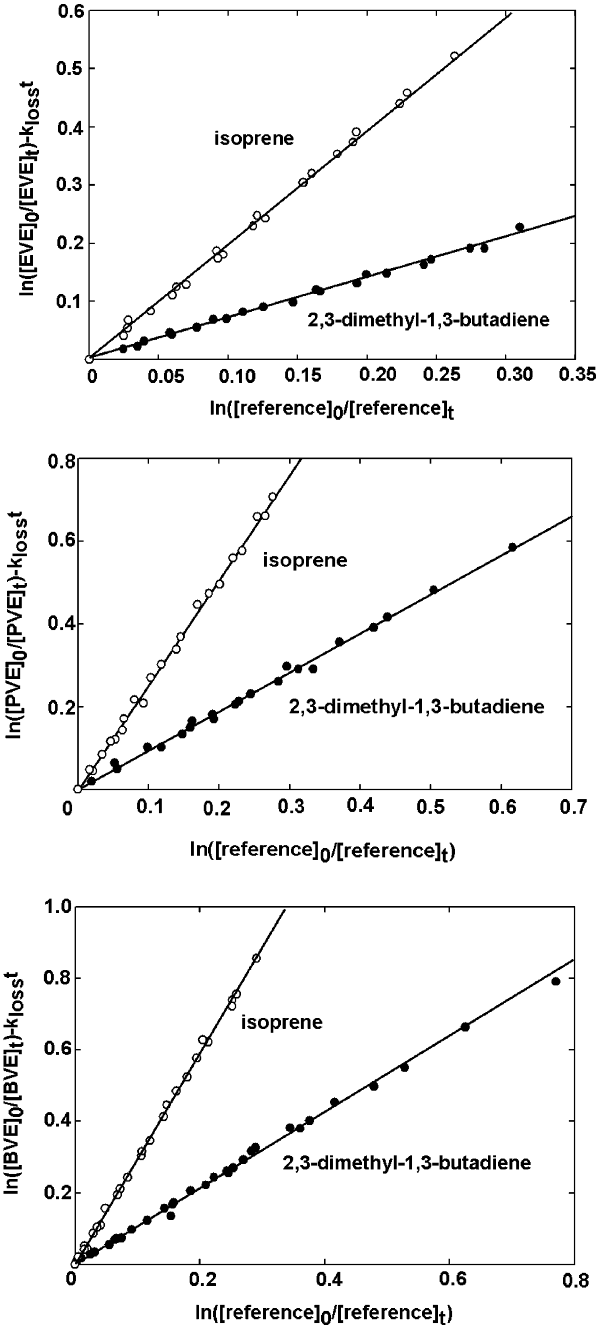

Figure 2. Plots of the kinetic data according to eq I for the gas-phase reaction of NO_3 radicals with (i) ethyl vinyl ether (EVE), (ii) propyl vinyl ether (PVE) and (iii) butyl vinyl ether (BVE). The plots have been labeled with the reference compound used.

As for the analogous OH radical reactions, the rate coefficients determined for NO_3 reactions show an increase with increasing carbon chain length with $k(\text{EVE}) < k(\text{PVE}) < k(\text{BVE})$, indicating that the order of reactivity of NO_3 toward alkyl vinyl ethers is similar to that observed for OH reactions. At the time of writing there were no other experimentally determined rate coefficients for the reactions of NO_3 with alkyl vinyl ethers reported in the literature with which to compare the values determined here. However, during the review process a relative rate kinetic study on the reaction of NO_3 with ethyl vinyl ether appeared by Pfrang et al.[35] in which they reported a value of $(1.7 \pm 1.3) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. They had

TABLE 3. Measured Rate Coefficient Ratios, k_1/k_2, and Rate Coefficients (in cm^3 Molecule^{-1} s^{-1}) for the Reactions of NO$_3$ with EVE, PVE and BVE Obtained in Present Work at 298 K Using the Relative Kinetic Technique

vinyl ether	reference	k_1/k_2	$10^{12}k_1$	av $10^{12}k$
EVE, $C_2H_5OCH{=}CH_2$	isoprene	1.99 ± 0.04	1.35 ± 0.28	1.40 ± 0.35
	2,3-dimethyl-1,3-butadiene	0.69 ± 0.02	1.45 ± 0.30	1.45 ± 0.30
PVE, $C_3H_7OCH{=}CH_2$	isoprene	2.54 ± 0.05	1.72 ± 0.35	1.85 ± 0.53
	2,3-dimethyl-1,3-butadiene	0.94 ± 0.02	1.98 ± 0.40	
BVE, n-$C_4H_9OCH{=}CH_2$	isoprene	2.94 ± 0.04	2.00 ± 0.40	2.10 ± 0.54
	2,3-dimethyl-1,3-butadiene	1.05 ± 0.02	2.20 ± 0.44	

considerable difficulties with the measurements, hence the large error limits, and concluded that the data would benefit from refinement. Considering the experimental difficulties encountered in the measurements by Pfrang et al. and the large scatter in their data points their measured value for NO$_3$ + EVE is in fair agreement with the value of (1.40 ± 0.35) × 10^{-12} cm^3 molecule^{-1} s^{-1} determined in this study lying just within our given error bar.

TABLE 4. Measured Rate Coefficient Ratios, k_1/k_2, and Rate Coefficients (in cm^3 Molecule^{-1} s^{-1}) for the Reactions of O$_3$ with EVE, PVE and BVE Obtained in the Present Work at 298 K Using the Relative Kinetic Technique

vinyl ether	reference	k_1/k_2	$10^{16}k_1$
EVE, $C_2H_5OCH{=}CH_2$	cyclohexene	2.56 ± 0.07	2.06 ± 0.42
PVE, $C_3H_7OCH{=}CH_2$	cyclohexene	2.89 ± 0.15	2.34 ± 0.48
BVE, n-$C_4H_9OCH{=}CH_2$	cyclohexene	3.20 ± 0.10	2.59 ± 0.52

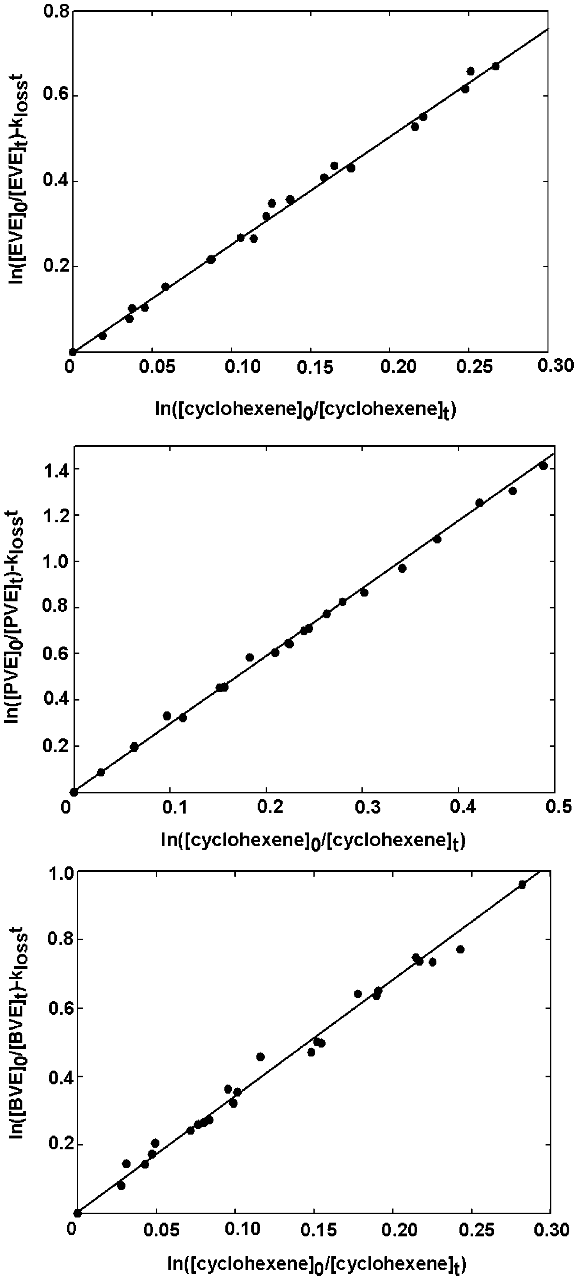

Figure 3. Plots of the kinetic data according to eq I for the gas-phase reaction of O$_3$ with (i) ethyl vinyl ether (EVE), (ii) propyl vinyl ether (PVE) and (iii) butyl vinyl ether (BVE). The plots have been labeled with the reference compound used.

Grosjean and Williams[22] have estimated a rate coefficient of 4.68 × 10^{-13} cm^3 molecule^{-1} s^{-1} for the reaction of NO$_3$ with MVE using SAR and LFER relationships. The rate coefficients determined here for the reactions of NO$_3$ with EVE, PVE and BVE are factors of 3−4.5 higher than the estimated value for NO$_3$ with MVE. Based on a comparison with the rate coefficients for the analogous OH radical reactions, where increases of between 2 and 3 are observed for the reactions of OH with EVE, PVE and BVE compared to OH + MVE, this seems fairly reasonable because NO$_3$ radical reactions with vinyl ethers appear to follow a trend similar to that observed for the OH radical reactions.

The rate coefficients for NO$_3$ with EVE, PVE and BVE are approximately 2 orders of magnitude higher than the corresponding rates for NO$_3$ with 1-butene, 1-pentene and 1-hexene, respectively.[12] Because the reactions are expected to proceed via electrophilic addition of NO$_3$ to the double bond, this comparison and the kinetic data obtained in this study are fully in line with (i) an expected increase in electron donation to the double bond with an increase in the carbon chain length of the RO entity and (ii) a much higher electron donating nature of alkoxy groups compared to alkyl groups.

In contrast to the analogue OH radical reactions the difference in the reactivity of the vinyl ethers toward electrophilc NO$_3$ addition compared to that of $CH_2{=}CH{-}CO{-}R$, $CH_2{=}CH{-}OC(O)R$ and $CH_2{=}CH{-}C(O)OR$ compounds is much starker. For the few compounds for which data are available[11,12,30−33,35,36] the rate coefficients for NO$_3$ with the vinyl ethers are an order of magnitude larger compared to $CH_2{=}CH{-}OC(O)R$ compounds and 3−4 orders of magnitude compared to $CH_2{=}CH{-}CO{-}R$ and $CH_2{=}CH{-}C(O)OR$ compounds.

O$_3$ Reaction. The rate constants for the reactions of ozone with EVE, PVE and BVE were measured relative to cyclohexene in the presence of an excess of cyclohexane to scavenge any OH radicals produced during the reactions. Figure 3 shows examples of the kinetic data for the three ethers plotted according to eq I. The rate coefficient ratios, k_1/k_2, obtained from these plots are listed in Table 4 and have been used in combination with k_2 (cyclohexene) = 8.1 × 10^{-17} cm^3

TABLE 5: Comparison of the Rate Coefficients (cm^3 $molecule^{-1}$ s^{-1}) Obtained in the Present Work at 298 K for the Reactions of O_3 with Selected Vinyl Ethers with Values Reported in the Literature Data for Other Vinyl Ethers at the Same Temperature

vinyl ether	$10^{16}k$	technique [ref]
EVE,	2.0 ± 0.2	concentration fit [23]
$C_2H_5OCH{=}CH_2$	1.54 ± 0.3	p-f-o kinetics [27][a]
	2.06 ± 0.42	this work
PVE,	2.4 ± 0.4	concentration fit [24]
$C_3H_7OCH{=}CH_2$	2.34 ± 0.48	this work
BVE,	2.9 ± 0.2	concentration fit [24]
n-$C_4H_9OCH{=}CH_2$	2.59 ± 0.52	this work
IBVE, i-$C_4H_9OCH{=}CH_2$	3.1 ± 0.2	concentration fit [24]
TBVE, t-$C_4H_9OCH{=}CH_2$	5.0 ± 0.5	concentration fit [24]

[a] Pseudo-first-order kinetic.

molecule^{-1} s^{-1} [30] to put the rate coefficients for the reaction of O_3 with EVE, PVE and BVE shown in Table 4 on an absolute basis. This results in rate coefficients for the reactions of O_3 with EVE, PVE and BVE (in units of cm^3 $molecule^{-1}s^{-1}$) of $k_1(O_3+EVE) = (2.06 \pm 0.42) \times 10^{-16}$, $k_1(O_3+PVE) = (2.34 \pm 0.48) \times 10^{-16}$ and $k_1(O_3+BVE) = (2.59 \pm 0.52) \times 10^{-16}$ at 298 K, respectively. The quoted errors are again the combination of the least squares standard 2σ deviations plus an additional 20% to account for uncertainties in the value of the reference rate coefficient.

The rate coefficients determined here for the reaction of O_3 with EVE, PVE and BVE are in excellent agreement with the values determined by Mellouki and co-workers[23,24] from a best fit to the concentration−time profiles measured in the EUPHORE chamber facility in Valencia, Spain (Table 5). Mellouki and co-workers[24] have also reported rate coefficients for the reaction of O_3 with other vinyl ethers, IBVE and TBVE, which are also listed in Table 5. Using a pseudo-first-order kinetic method, Grosjean and Grosjean[27] have determined a rate coefficient of $(1.54 \pm 0.3) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} for the reaction of O_3 with EVE that is somewhat lower than the value of both our determination and that of Thiault et al.[23] The value of Grosjean and Grosjean, however, does agree within the combined reported error limits of the other studies.

Although in the ozonolysis of alkyl vinyl ethers there is a tendency toward higher rate coefficients with increase in the carbon chain length with EVE < PVE < BVE < IBVE < TBVE, the increase from EVE to BVE is much less pronounced than that observed for the reactions of OH and NO_3 radicals with the ethers. A very similar reactivity pattern has been observed for the reaction of ozone with the corresponding alkenes;[12] however, the rate coefficients for the ozonolysis of the vinyl ethers are much higher than those of the corresponding alkenes. This again reflects the strong electron donating effect of alkoxy groups to the carbon−carbon double bond, which facilities the electrophilic addition of ozone to the double bond. The rate coefficients for the reactions of ozone with the vinyl ethers are around 2 orders of magnitude larger than those reported in the literature for the corresponding $CH_2{=}CH{-}CO{-}R$, $CH_2{=}CH{-}OC(O)R$ and $CH_2{=}CH{-}C(O)OR$ compounds.[11,12,30,32]

Many types of correlations of kinetic data have been applied to highlight trends in chemical behavior and also to predict the rate coefficient for the reaction of a compound with species such as OH, NO_3 and O_3 for which experimental data do not exist. For example, rate coefficients for the reactions of OH and NO_3 radicals with unsaturated organic compounds have often been correlated with the first vertical ionization potentials (E_v) of the compounds,[36] whereby the logarithm of the rate coefficient for the particular reaction is plotted as a function of the corresponding E_v. Other types of correlation that are typically applied and are known as "linear free energy relationships" involve plotting the logarithm of the rate coefficient for reaction of the compound with, for example, OH ($\log(k_{OH})$), against the logarithm of the rate coefficient values for the corresponding reactions with another species, e.g., NO_3 ($\log(k_{NO_3})$).[36] However, often the data set for the reactions of species such as OH, NO_3 and O_3 with organic compounds is not sufficiently wide to be able to make recommendations concerning the rate coefficients for many of the reactions. Ionization potentials could not be found in the literature for the vinyl ethers. The number of available rate coefficients for the reactions of OH and NO_3 radicals with the vinyl ethers is too small for a meaningful "linear free energy relationship"; however, a plot with the few available values suggests that a reasonably linear relationship exists between these reactants for C1 to C4 alkyl vinyl ethers.

It has been shown in recent years that it is possible to predict the rate coefficients for the reactions of OH, NO_3 and O_3 with alkenes by perturbation frontier molecular orbital (PFMO) theory.[37−40] The natural logarithm of the room-temperature rate coefficients have been shown to correlate with the energy change, ΔE, when the highest occupied molecular orbital (HOMO) of the alkene perturbs the singly occupied molecular orbital (SOMO) for the OH and NO_3 radical or the lowest unoccupied molecular orbital (LUMO) for O_3 as two reactant orbitals overlap. To the best of our knowledge this predictive technique has only been applied to unsubstituted alkenes[37,39] and chloroalkenes[38] and not to oxygenated alkenes. It would be interesting to extend the technique to the available database on oxygenated alkenes. Unfortunately, our group does not presently have the computer programs to calculate the HOMO and SOMO energies necessary for the correlations.

Atmospheric Implication

The rate coefficients determined in this study for the reactions of OH and NO_3 radicals and O_3 with EVE, PVE and BVE can be used to estimate the atmospheric lifetimes of these selected vinyl ethers with respect to degradation by these species. The lifetime τ is defined as $1/k$[species], where k is the rate constant for the reaction of the reactive species (OH, NO_3 or O_3) with vinyl ethers determined in this study and [species] is the concentration of the reactive species. The average tropospheric concentrations of OH and NO_3 radicals and ozone used in calculations of the lifetimes were ca. 1.6×10^6 (12 h daytime average[41]), 5×10^8 (12 h nighttime average[42,43]) and 7×10^{11} (24 h average concentration[44]) molecule cm^{-3}, respectively. These are the values typically used in publications presenting calculations of the lifetimes of organic compounds with respect to reactions with OH, NO_3 and O_3. The atmospheric concentrations of NO_3 radicals, however, can be highly variable.[43]

The atmospheric lifetimes of EVE, PVE and BVE with respect to reactions with OH, NO_3 and ozone shown in Table 6 range from approximately 15 min for the reactions of NO_3 with vinyl ethers to a few hours for the reactions with OH. Thus all three loss processes can make significant contributions to the degradation of EVE, PVE and BVE. The short lifetimes of the vinyl ethers show that they will be quickly degradated when emitted to the atmopshere and will only be actively involved in tropospheric chemistry on local to regional scales. Work within the EU project MOST[45] has shown that the photolysis of vinyl ethers is a negligible loss process for this class of organic compound in the troposphere.

TABLE 6: Estimated Atmospheric Lifetime (h) of Ethyl Vinyl Ether (EVE), Propyl Vinyl Ether (PVE) and Butyl Vinyl Ether (BVE) with Respect to Degradation by OH and NO_3 Radicals and Ozone[a]

vinyl ether	t_{OH}	t_{NO_3}	t_{O3}
EVE, $C_2H_5OCH{=}CH_2$	2.2	0.40	1.9
PVE, $C_3H_7OCH{=}CH_2$	1.8	0.30	1.7
BVE, n-$C_4H_9OCH{=}CH_2$	1.5	0.27	1.5

[a] Based on the average tropospheric concentrations of OH and NO_3 radicals and ozone of ca. 1.6×10^6 (12 h daytime average[41]), 5.4×10^8 (12 h nighttime average[42,43]) and 7×10^{11} (24 h average concentration[44]) molecule cm^{-3}, respectively.

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