Rate Coefficients for the Gas-Phase Reactions of OH and NO_3 Radicals and O_3 with Ethyleneglycol Monovinyl Ether, Ethyleneglycol Divinyl Ether, and Diethyleneglycol Divinyl Ether

Shouming Zhou,[†,‡,§] Ian Barnes,[*,‡] Tong Zhu,[†] and Thorsten Benter[‡]

State Key Joint Laboratory for Environmental Simulation and Pollution Control, College of Environmental Science, Peking University, 100871 Beijing, China, and Bergische Universitaet Wuppertal, Physikalische Chemie/FBC, Gauss Strasse 20, D-42119 Wuppertal, Germany

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Kinetic studies have been performed on the reactions of OH and NO_3 radicals and ozone with three ethyleneglycol vinyl ethers (EGVEs), that is, ethyleneglycol monovinyl ether (EGMVE, $HOCH_2CH_2OCH{=}CH_2$), ethyleneglycol divinyl ether (EGDVE, $H_2C{=}CHOCH_2CH_2OCH{=}CH_2$), and diethyleneglycol divinyl ether (DEGDVE, $H_2C{=}CHOCH_2CH_2OCH_2CH_2OCH{=}CH_2$). Using a relative rate technique, rate coefficients have been determined for the reactions in a 405 L borosilicate glass chamber at (298 ± 3) K in one atmosphere of synthetic air using in situ FTIR spectroscopy to monitor the reactants. The following rate coefficients (in units of $cm^3\ molecule^{-1}\ s^{-1}$) were obtained: $(1.04 \pm 0.22) \times 10^{-10}$, $(1.23 \pm 0.33) \times 10^{-10}$, and $(1.42 \pm 0.30) \times 10^{-10}$ for the reaction of OH with EGMVE, EGDVE, and DEGDVE, respectively; $(2.23 \pm 0.46) \times 10^{-12}$, $(1.95 \pm 0.50) \times 10^{-12}$, and $(6.14 \pm 1.38) \times 10^{-12}$ for the reaction of NO_3 with EGMVE, EGDVE, and DEGDVE, respectively; and $(2.02 \pm 0.41) \times 10^{-16}$, $(1.69 \pm 0.41) \times 10^{-16}$, and $(2.70 \pm 0.56) \times 10^{-16}$ for ozonolysis of EGMVE, EGDVE, and DEGDVE, respectively. Using the kinetic rate data, tropospheric lifetimes for EGMVE, EGDVE, and DEGDVE with respect to their reactions with OH, NO_3, and ozone have been estimated for typical ambient air concentrations of these oxidants.

Introduction

A wide range of oxygenated organic compounds have been found 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 troposphere as a result of the atmospheric oxidation 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 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,[11−13] information on the gas-phase reactions of oxygenated organic compounds is currently limited to a relatively small range of compounds.[14−17]

Vinyl ethers ($ROCH{=}CH_2$) are released to the atmosphere entirely from anthropogenic sources. These ethers are widely used in industry as oxygenated solvents, additives, and in different types of coatings.[18,19] To date, studies on the atmospheric chemistry of vinyl ethers have not been very extensive. Limited data are available in the literature on the gas-phase reactions of a few alkyl vinyl ethers.[7,9,20−32] As part of the research work in this laboratory on the atmospheric chemistry of oxygenated hydrocarbons,[26,27] we report here first-time determinations of the rate coefficients for the reactions of OH and NO_3 radicals and ozone with three ethyleneglycol vinyl ethers (EGVEs), that is, ethyleneglycol monovinyl ether (EGMVE, $HOCH_2CH_2OCH{=}CH_2$), ethyleneglycol divinyl ether (EGDVE, $H_2C{=}CHOCH_2CH_2OCH{=}CH_2$), and diethyleneglycol divinyl ether (DEGDVE, $H_2C{=}CHOCH_2CH_2OCH_2CH_2OCH{=}CH_2$).

Experimental Methods

All of the experiments were performed in a 405 L borosilicate glass chamber at 298 ± 3 K and 750 ± 20 Torr total pressure of synthetic air. The reactor is equipped with 18 fluorescent lamps (Philips TLA40W/05; $\lambda_{max} = 360$ nm) and three low-pressure mercury vapor lamps (Philips TUV40W; $\lambda_{max} = 254$ nm), which are used for the photolytic production of radicals. A detailed description of the chamber can be found elsewhere.[33] A White-type mirror system mounted within the chamber and coupled to an FTIR spectrometer enables in situ infrared monitoring of the reactants. The White system was operated with a total optical absorption path of 50.4 m, and infrared spectra were recorded with a spectral resolution of 1 cm^{-1}.

Rate coefficients for the reactions of OH and NO_3 radicals and O_3 with the EGVEs were determined using a relative rate method in which the relative disappearance rates of the EGVEs and reference compound(s), whose rate coefficient(s) with the reactive species (OH, NO_3, or O_3) is(are) reliably known, were measured in the presence of either OH, NO_3, or O_3, for example, for the OH radical studies:

$$\text{EGVE} + \text{OH} \rightarrow \text{products},\ k_1 \qquad \text{(R1)}$$

$$\text{reference} + \text{OH} \rightarrow \text{products},\ k_2 \qquad \text{(R2)}$$

Additionally, the EGVEs and the reference hydrocarbon(s) could be lost by deposition to the reactor walls or photolysis. When EGDVE and DEGDVE were admitted into the chamber in the

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[*] Corresponding author. Phone: +49 202 439 2510. Fax: +49 202 439 2505. E-mail: barnes@uni-wuppertal.de.

[†] Peking University.

[‡] Bergische Universitaet Wuppertal.

[§] Present address: Department of Chemistry and Environmental Research Institute, University College Cork, Ireland.

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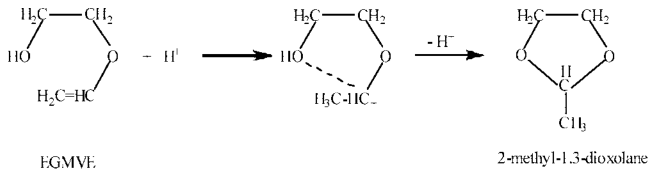
TABLE 1: OH Radical Source, Reference Compounds Used, Measured Rate Coefficient Ratios, k_1/k_2, and Values of the Rate Coefficients k_1 (in cm^3 $molecule^{-1}$ s^{-1}) Obtained at 298 K in 750 Torr of Synthetic Air in the Present Work for the Reactions of OH Radical with EGMVE, EGDVE, and DEGDVE Using the Relative Kinetic Technique

EGVEs	OH source	reference	k_1/k_2	$k_1 \times 10^{10}$	average $k_1 \times 10^{10}$
EGMVE $CH_2{=}CHOCH_2CH_2OH$	H_2O_2	TMB[a]	1.83 ± 0.05	1.04 ± 0.22	1.04 ± 0.22
EGDVE $H_2C{=}CHOCH_2CH_2OCH{=}CH_2$	H_2O_2	TMB[a]	2.28 ± 0.05	1.29 ± 0.27	1.23 ± 0.33
		isoprene	1.24 ± 0.05	1.25 ± 0.26	
DEGDVE $H_2C{=}CHOCH_2CH_2OCH_2CH_2OCH{=}CH_2$	CH_3ONO + NO	isobutene	2.78 ± 0.10	1.43 ± 0.29	1.42 ± 0.30
		isoprene	1.41 ± 0.04	1.42 ± 0.29	

[a] TMB-1,3,5-trimethybenzene.

dark, in addition to wall loss, the compounds were also observed to decay with the formation of products as evidenced by the appearance of new bands in the recorded IR spectra. Several of the new bands could be assigned to acetaldehyde (CH_3CHO). Similar behavior was observed in an earlier study on alkyl vinyl ethers from this laboratory in which CH_3CHO and the corresponding alcohol from the breakdown of the alkyl vinyl ethers were identified.[26] The decomposition of the alkyl vinyl ethers observed in the earlier study was attributed to acid-catalyzed hydrolysis of the compounds at the reactor walls, and it is assumed that this is also the case for EGDVE and DEGDVE in the present study. When EGMVE was introduced into the reactor wall loss and decomposition was also observed, however, in this case only one product was formed, which has been identified as 2-methyl-1,3-dioxolane. The formation of this compound is attributed to acid-catalyzed hydrolysis at the reactor walls via a five-member ring intermediate:



The combined dark decomposition and wall loss were found to obey first-order kinetics and can be represented by:

$$\text{EGVE (dark decay and wall loss)} \rightarrow \text{products}, k_3 \quad \text{(R3)}$$

$$\text{reference (dark decay and wall loss)} \rightarrow \text{products}, k_4 \quad \text{(R4)}$$

Test experiments showed that loss through photolysis was negligible for the EGVEs and the reference compounds used in the experiments for both the visible fluorescence and the UV lamps.

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

$$\ln\left\{\frac{[\text{EGVE}]_{t0}}{[\text{EGVE}]_t}\right\} - k_3(t-t_0) = \frac{k_1}{k_2}\times\left(\ln\left\{\frac{[\text{reference}]_{t0}}{[\text{reference}]_t}\right\} - k_4(t-t_0)\right) \quad \text{(I)}$$

where t_0 is the time at which the reaction is initiated; t is the time at which the IR spectrum was recorded; $[\text{EGVE}]_{t0}$ and $[\text{reference}]_{t0}$ are the concentrations of the EGVE and reference compound, respectively, at time t_0; $[\text{EGVE}]_t$ and $[\text{reference}]_t$ are the corresponding concentrations at time t; k_1 and k_2 are the rate coefficients for the reactions of the EGVE and reference with OH radicals, respectively; and k_3 and k_4 are the dark loss rate of the EGVE and reference compound. Values of k_3 were typically 3×10^{-4}, 8×10^{-5}, and 9×10^{-5} s^{-1} for EGMVE, EGDVE, and DEGDVE, respectively. The value of k_4 for most references was negligibly small; a correction was only needed when 1,3,5-trimethylbenzene (TMB) was used as the reference compound: the average value of k_4 in such cases was 5×10^{-5} s^{-1}. Plots of $\ln([\text{EGVE}]_{t0}/[\text{EGVE}]_t) - k_3(t - t_0)$ versus $\ln([\text{reference}]_{t0}/[\text{reference}]_t - k_4(t - t_0)$ should give straight lines with a slope k_1/k_2. The absolute rate coefficient k_1 can be derived from the rate coefficient ratio k_1/k_2 using the known rate coefficient k_2. In the OH kinetic experiments, typically 60 interferograms were coadded per spectrum, resulting in a scanning time of 60 s per spectrum, and 15−20 spectra were recorded for each experiment over periods of between 20 and 30 min.

The rate coefficients for the reactions of NO_3 radicals and ozone with the EGVEs have been determined in a manner similar to that described above for the OH reactions.

OH Radical Reaction. The photolysis of either H_2O_2 (R5) or CH_3ONO in the presence of NO (R6−R8) was used for the production of OH radicals:

$$H_2O_2 + h\nu\ (\lambda_{max} = 254\ \text{nm}) \rightarrow 2OH \quad \text{(R5)}$$

$$CH_3ONO + h\nu\ (\lambda_{max} = 360\ \text{nm}) \rightarrow CH_3O + NO \quad \text{(R6)}$$

$$CH_3O + O_2 \rightarrow CH_2O + HO_2 \quad \text{(R7)}$$

$$HO_2 + NO \rightarrow NO_2 + HO \quad \text{(R8)}$$

The EGVEs and other liquid compounds were added to the reactor at reduced pressure by injection into a heated inlet port, which was flushed with dry synthetic air. Gaseous compounds were injected directly into the chamber using gastight syringes and mixed by turning on the fans installed in the chamber. The initial concentrations of the EGVEs and reference compounds were approximately 5.0 ppm (1 ppm = 2.46×10^{13} molecule cm^{-3} at 298 K and 1 atm) and 4.9−5.5 ppm, respectively, and those of CH_3ONO, NO, and H_2O_2 were 1.5−4.0, 9.8−19.8, and ∼20 ppm, respectively. NO was added to the CH_3ONO reaction mixture to suppress the formation of O_3 and NO_3 radicals. Because of the overlap of the IR absorption of EGMVE and EGDVE with CH_3ONO, H_2O_2 was used as OH radical precursor in the EGMVE and EGDVE rate measurements. The reactants were monitored in the infrared at the following wavenumbers (in cm^{-1}): EGMVE at 3131; EGDVE at 3127; DEGDVE at 1617.2; isobutene at 890; isoprene at 893.4 and 905.9; and TMB at 836.

NO_3 Radical and Ozone Reactions. NO_3 radicals were produced by the thermal dissociation of N_2O_5 prepared in solid form according to a literature method:[34]

$$N_2O_5 + M \rightarrow NO_3 + NO_2 + M \quad \text{(R9)}$$

Ozone was generated as a mixture in O_2 by passing O_2 through an ozone generator.

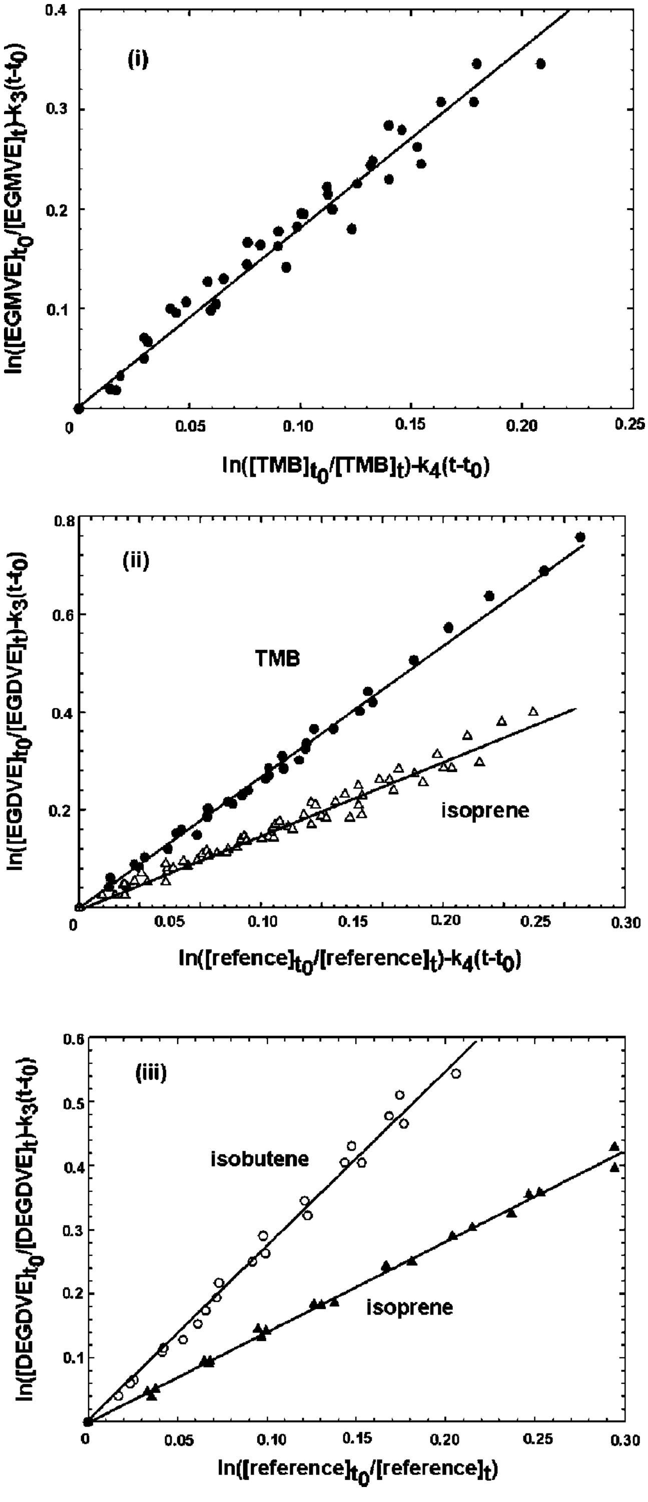


Figure 1. Plots of the kinetic data according to eq I for the gas-phase reaction of OH radicals with (i) EGMVE, (ii) EGDVE, and (iii) DEGDVE.

The experiments on the reactions of NO_3 with EGVEs were performed by multiple additions of N_2O_5 to a mixture of EGVEs 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 reactions of ozone with the EGVEs, ozone was added stepwise to premixed mixtures containing the EGVEs, cyclohexane, and the reference organic. The cyclohexane was present in an excess sufficient to scavenge more than 95% of any OH radicals produced in the reaction system.

The initial concentrations of the reactants for the NO_3 experiments were approximately EGVEs 5.0 ppm, reference hydrocarbons 4.8−5.5 ppm; and for the ozone experiments they were EGVEs 2.7−5.5 ppm, reference hydrocarbons 3.8−7.3 ppm, O_3 1.0−1.8 ppm, cyclohexane 290 ppm. The reactants used in the experiments were monitored at the following wavenumbers (in cm^{-1}): EGMVE at 1622.2; EGDVE at 1619.7; DEGDVE at 1617.2; cyclohexene at 1139.7; *trans*-2-butene at 962.7 and 973.8; isoprene at 893.4 and 905.9; 2,3-dimethyl-1,3-butadiene at 895; and 1,3-cycloheptadiene at 1442.

Results and Discussion

OH Radical Reaction. Table 1 lists the OH radical sources and reference compounds used in the OH radical kinetic measurements. Examples of the kinetic data for all three EGVEs, plotted according to eq I, are shown in Figure 1. The rate coefficient ratios k_1/k_2 obtained from such plots for a minimum of three experiments are also listed in Table 1. Rate coefficients, k_1, for the reactions of OH with EGMVE, EGDVE, and DEGDVE, put on an absolute basis using $k_2(\mathrm{OH} + \mathrm{TMB}, 298\ \mathrm{K}) = (5.67 \pm 1.13) \times 10^{-11}$, $k_2(\mathrm{OH} + \mathrm{isobutene}, 298\ \mathrm{K}) = (5.14 \pm 1.03) \times 10^{-11}$, and $k_2(\mathrm{OH} + \mathrm{isoprene}, 298\ \mathrm{K}) = (1.01 \pm 0.20) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} as recommended in Calvert et al. with a 20% uncertainty,[12,13] are also listed in Table 1. The corrections to the data for dark losses of the EGVEs were approximately 40% for EGMVE and 15% for both EGDVE and DEGDVE. The dark loss for EGMVE is much higher than those of EGDVE and DEGDVE; this difference may be due to a more efficient acid-catalyzed hydrolysis of EGMVE via a cyclic intermediate as compared to EGDVE and DEGDVE. In addition, EGMVE has a terminal −OH group, which may result in better retention of the compound at the reactor surfaces through hydrogen bonding. The dark loss rate was very dependent on the acidic nature of the chamber surface and is the reason for the observed variations from experiment to experiment and between reaction system to reaction system, that is, OH, NO_3, or O_3. Checks were frequently made to check that the dark loss rate did not change between the start and termination of the experiments. The quoted errors of the rate coefficients k_1 are a combination of the least-squares standard deviations 2σ plus an additional 20% to cover uncertainties in the values of the reference rate coefficients.

As can be seen in Figure 1, good linear relationships were found for all three EGVEs, and there is also good agreement between the rate coefficient values obtained using two different reference compounds for EGDVE and DEGDVE (Table 1). For the reaction of OH with EGMVE, a value of $k_1(\mathrm{OH} + \mathrm{EGMVE}) = (1.04 \pm 0.22) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} has been obtained at 298 K using a single reference compound. For the reactions of OH with EGDVE and DEGDVE, two reference compounds were employed. Because there is very good agreement between the values obtained with the different reference compounds, we prefer to quote rate coefficients for the reactions that are averages of both determinations. Averaging the values of the rate coefficients and taking errors that encompass the extremes of both determinations for each reaction gives rate coefficients at 298 K of $k_1(\mathrm{OH} + \mathrm{EGDVE}) = (1.23 \pm 0.33) \times 10^{-10}$ and $k_1(\mathrm{OH} + \mathrm{DEGDVE}) = (1.42 \pm 0.30) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}.

To the best of our knowledge, there are no other experimentally determined rate coefficients for the reactions of OH with the EGVEs presently available in the literature with which the values determined in this work can be compared. Rate coef-

TABLE 2: Comparison of the Rate Coefficients (in cm^3 $molecule^{-1}$ s^{-1}) for the Reactions of OH with EGVEs with Values Reported in the Literature for Unsaturated Organic Compounds and That for OH Abstraction from the Alkyl Group in EGVEs at the Same Temperature

EGVEs ($k \times 10^{11}$)[a]		unsaturated organics ($k \times 10^{11}$)		estimated H-atom abstraction rate ($k \times 10^{11}$)[c]	
EGMVE $CH_2{=}CHOCH_2CH_2OH$	10.4	3-buten-1-ol $CH_2{=}CHCH_2CH_2OH$	5.5[b]	EGMVE $HOCH_2CH_2OCH{=}CH_2$	1.4
EGDVE $H_2C{=}CHOCH_2CH_2OCH{=}CH_2$	12.3	1,5-hexadiene $CH_2{=}CHCH_2CH_2{-}CH{=}CH_2$	6.2[c]	EGDVE $H_2C{=}CHOCH_2CH_2OCH{=}CH_2$	1.9
DEGDVE $H_2C{=}CHOCH_2CH_2OCH_2CH_2OCH{=}CH_2$	14.2			DEGDVE $H_2C{=}CHOCH_2CH_2OCH_2CH_2OCH{=}CH_2$	3.9

[a] This work. [b] Reference 37. [c] Estimated from structure−activity relationships given in Kwok et al.[36]

TABLE 3: Reference Compounds Employed, Measured Rate Coefficient Ratios, k_1/k_2, and Rate Coefficients k_1 (in cm^3 $molecule^{-1}$ s^{-1}) Obtained in the Present Work at 298 K for the Reactions of the NO_3 Radical with EGMVE, EGDVE, and DEGDVE Using the Relative Kinetic Technique

EGVEs	reference	k_1/k_2	$k_1 \times 10^{12}$	average $k_1 \times 10^{12}$
EGMVE $HOCH_2CH_2OCH{=}CH_2$	2,3-dimethyl-1,3-butadiene	1.06 ± 0.05	2.23 ± 0.46	2.23 ± 0.46
EGDVE $H_2C{=}CHOCH_2CH_2OCH{=}CH_2$	isoprene	2.73 ± 0.04	1.85 ± 0.38	1.96 ± 0.50
	2,3-dimethyl-1,3-butadiene	0.98 ± 0.02	2.06 ± 0.41	
DEGDVE $H_2C{=}CHOCH_2CH_2OCH_2CH_2OCH{=}CH_2$	2,3-dimethyl-1,3-butadiene	2.89 ± 0.12	6.07 ± 1.24	6.14 ± 1.38
	1,3-cycloheptadiene	0.96 ± 0.05	6.21 ± 1.31	

ficients for the OH radical reactions have been estimated using the AOPWIN program,[35] which is based upon the structure−activity relationship (SAR) method described in Kwok et al.[36] The program predicts rate coefficients of 4.54×10^{-11}, 8.24×10^{-11}, and 9.64×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the reactions of OH with EGMVE, EGDVE, and DEGDVE, respectively. The predicted values are all slightly lower than the measured values by factors of 2.29, 1.48, and 1.47 for EGMVE, EGDVE, and DEGDVE, respectively, which is satisfactory for the type of estimation method used. The program predicts the reactivity trend shown by the measurements, that is, $k(OH + EGMVE) < k(OH + EGDVE) < k(OH + DEGMVE)$.

In Table 2, the rate coefficients for the reactions of OH with the EGVEs are compared to the rate coefficients of some structurally similar unsaturated oxygenates. Table 2 also lists rate coefficients for H-atom abstraction from the $-OCH_2CH_2O-$ groups in the EGVEs, which were estimated using the SAR outlined by Kwok et al.[36] for oxygenated organics, assuming that the $-OCH{=}CH_2$ group has the same substituted factor as a simple ether $-OR$ (R = alkyl), which might not necessarily be correct.

A number of rate coefficients have been reported for the reactions of OH with unsaturated alcohols.[36−39] Papagni et al.[38] established that the rate coefficients they measured for the reactions of OH with three unsaturated alcohols were between 1.8−2.1 times higher than those of OH with the corresponding alkenes. This is somewhat higher than the substituent group factor of ~1.6 for $-CH_2OH$ recommended by Kwok et al.[36] More recently, Imamura et al.[37] have reported substituent factors between 1.6 and 2.1 for unsaturated alcohols and state that their substituent factors are consistent with those observed by Papagni et al.[38] The 298 K rate coefficient determined here for OH with EGMVE is a factor of 1.89 higher than that of OH with the corresponding unsaturated alcohol 3-buten-1-ol (5.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, Table 2)[37] and a factor of 3.3 larger than that of OH with the corresponding alkene, 1-butene (3.14×10^{-11} cm^3 $molecule^{-1}$ s^{-1}).[15] Therefore, the $-OCH_2CH_2OH$ group is activating the $CH_2{=}CH-$ bond toward OH radical addition more strongly than is the $-CH_2CH_2OH$ group. This is not surprising because the lone pairs on the ether oxygen atom are known to greatly enhance electrophilic radical additions at double bonds.[9] For the reaction of OH with EGDVE, an enhancement of 1.98 is observed over the estimated rate coefficient of OH with the diene 1,5-hexadiene (6.2×10^{-11} cm^3 $molecule^{-1}$ s^{-1}, Table 2).[36]

EGMVE ($CH_2{=}CHOCH_2CH_2OH$) is structurally similar to ethyl vinyl ether (EVE, $CH_2{=}CHOCH_2CH_3$), the only difference being substitution of one of the methyl H-atoms in the $-CH_2CH_3$ group of EVE by an $-OH$ group. A rate coefficient of $(7.3 \pm 0.9) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} has been reported by this laboratory for the reaction of OH with EVE at 298 K.[26] Thus, the rate coefficient for the reaction of OH with EGMVE measured in this study (see Table 1) is about a factor of 1.4 higher than that reported for OH with EVE. This observation and the comparisons made above with the reactions of OH with 3-buten-1-ol and 1-butene suggest that in the reaction of OH with EGMVE both the ether and the alcohol functionalities in the $-OCH_2CH_2OH$ unit play a role in activating the $CH_2{=}CH-$ bond toward OH radical addition.

Unfortunately, there are no other rate coefficients for alkyl glycol mono vinyl ethers available to validate this single observation. However, because EGMVE, alkyl vinyl ethers, unsaturated alcohols, and alkenes all react with OH by a similar reaction mechanism, that is, OH radical addition to the carbon−carbon double bond and H-abstraction from alkyl groups in the compounds, with OH addition dominating (see Table 2 for estimated H-atom contribution), it seems reasonable to assume that the rate coefficients for the reactions of OH radicals with other alkyl glycol mono vinyl ethers will be similarly enhanced as compared to those of the structurally analogous alkyl vinyl ethers.

The rate coefficient for the reaction of OH with EGDVE is higher than that of OH with EGMVE, which is to be expected because EGDVE contains two carbon−carbon double bonds. However, the rate coefficient for the reaction of OH with EGDVE is higher than that of OH with EGMVE by only 1.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1}; this difference is much less than what one would predict using SAR for the presence of a second double bond. The AOPWIN program, [35] for example, predicts that the rate coefficient for the reaction of OH with EGDVE should be approximately twice that of OH with EGMVE. For monoalkenes and dialkenes, the rate coefficients for reactions of the OH radical with dialkenes are almost a factor of 2 higher than those of the structurally similar monoalkenes.[15] At present,

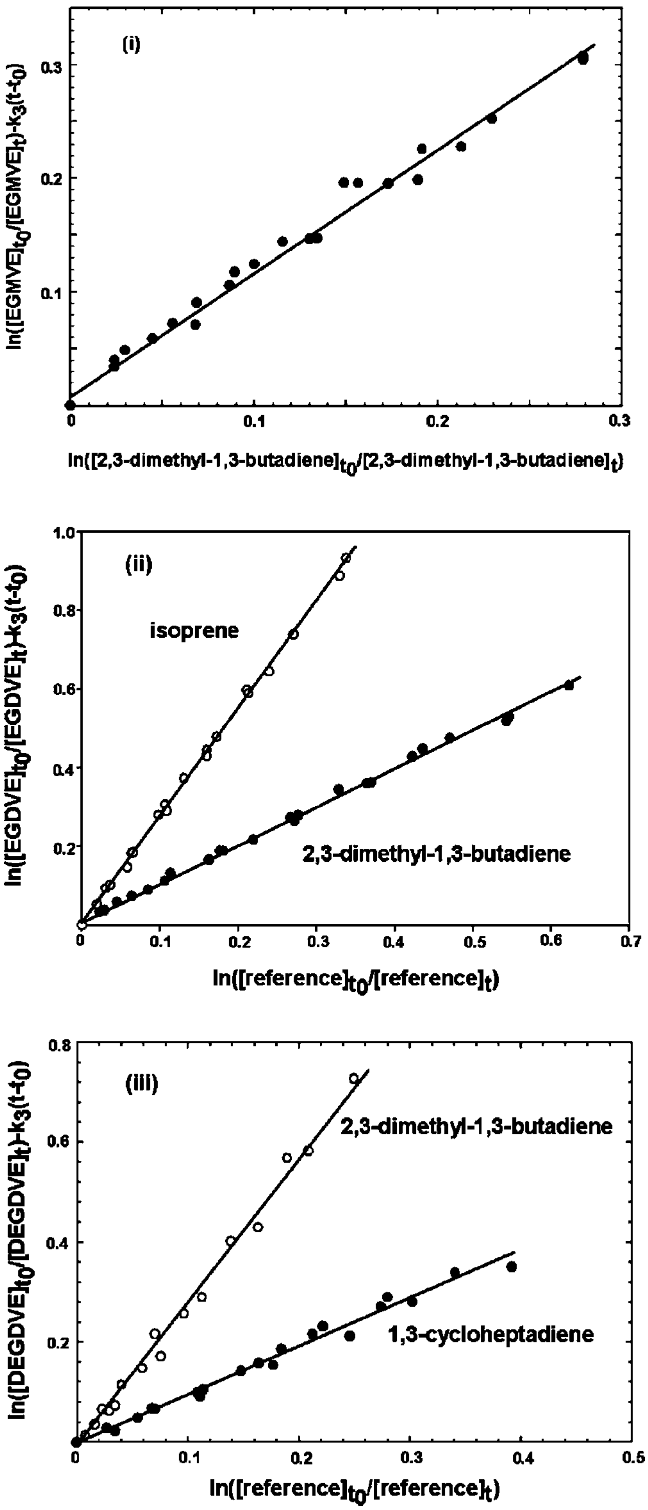


Figure 2. Plots of the kinetic data according to eq I for the gas-phase reaction of NO_3 radicals with (i) EGMVE, (ii) EGDVE, and (iii) DEGDVE.

we have no explanation for this; it is possibly because the reactions of OH with the EGVEs are already very fast, that is, approaching collision controlled, and the principles of the SAR estimation technique may no longer strictly apply.

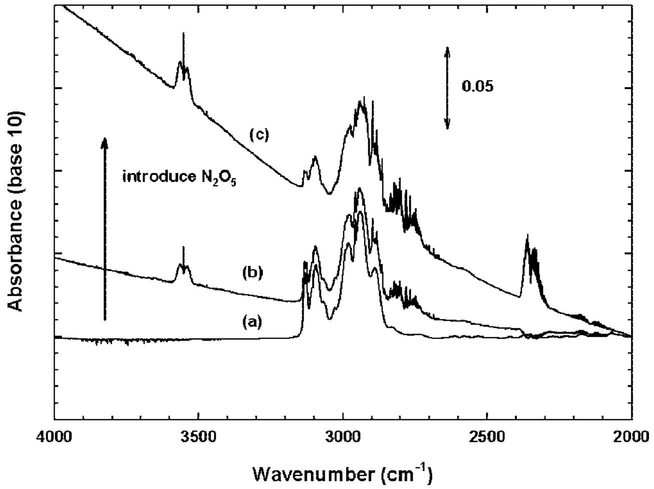


Figure 3. Baseline elevation in study of the NO_3 radical reaction with EGDVE: (a) before introduction of N_2O_5; (b) after introduction of N_2O_5 for 5 min; and (c) after introduction of N_2O_5 for 8 min.

It can be seen from Table 2 that the SAR estimations predict that H-atom abstraction from EGVEs can occur to a fairly significant extent, with this process accounting for between 14% and 27% of the overall OH radical reactions with the EGVEs. However, product studies for each EGVE are needed to verify the magnitude of this H-atom abstraction channel. Interestingly, the rate coefficient for DEGDVE is higher than that of EGDVE by 1.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1}; this matches perfectly the difference of 2.0×10^{-11} cm^3 $molecule^{-1}$ s^{-1} between the estimated H-atom abstraction contributions to the overall reaction rate for DEGDVE and EGDVE.

FTIR spectroscopy has been used to study the reactions presented here, and product information will obviously be contained in the recorded spectra. However, all of the investigations were performed in the presence of a reference compound, and the IR spectra of the products from the decay of the reference compound will be superimposed on the IR spectra from the products of the reaction of OH with the EGVEs. In addition, most of the expected products are not commercially available and would need to be synthesized for positive identification and quantization. From work published on the products from the reactions of OH, NO_3, and O_3 with alkyl vinyl ethers, it is known that addition of the reactants to the double bond results to a large extent in a splitting of the double bond with the formation of an organic formate (ROCH(O)) and a corresponding aldehyde in high yield in all cases.[26,27]

For example, the reaction of OH at the double bond in EGMVE would be expected to produce 2-hydroxyethylformate ($HOCH_2CH_2OC(O)H$) and formaldehyde among other products. Abstraction of an H-atom in the glycol $-CH_2CH_2-$ unit in EGMVE could potentially produce products such as vinyl formate ($CH_2{=}CHOC(O)H$) or vinyl-2-hydroxyacetate ($HOCH_2C(O)OCH{=}CH_2$). All of the products will have fairly similar carbonyl absorptions, and without calibrated reference spectra identification by visual inspection of the spectra is problematic. Therefore, until more information from kinetic and detailed product studies on this type of compound becomes available, further speculation on the relative contribution of the possible reaction pathways is currently unwarranted.

NO_3 Radical Reaction. Figure 2 shows examples of the kinetic data for the reaction of NO_3 with all three EGVEs plotted according to eq I. Good linear correlations were obtained for all three compounds. The corrections for the contribution of the combined dark wall and decomposition losses of the EGVEs to the measured overall losses were approximately 40−50% for EGMVE and 10−15% for both EGDVE and DEGDVE. The reference hydrocarbons employed and the rate coefficient ratios, k_1/k_2, obtained from the plots of the data as exemplified in Figure 2 are listed in Table 3. Using these ratios in combination with

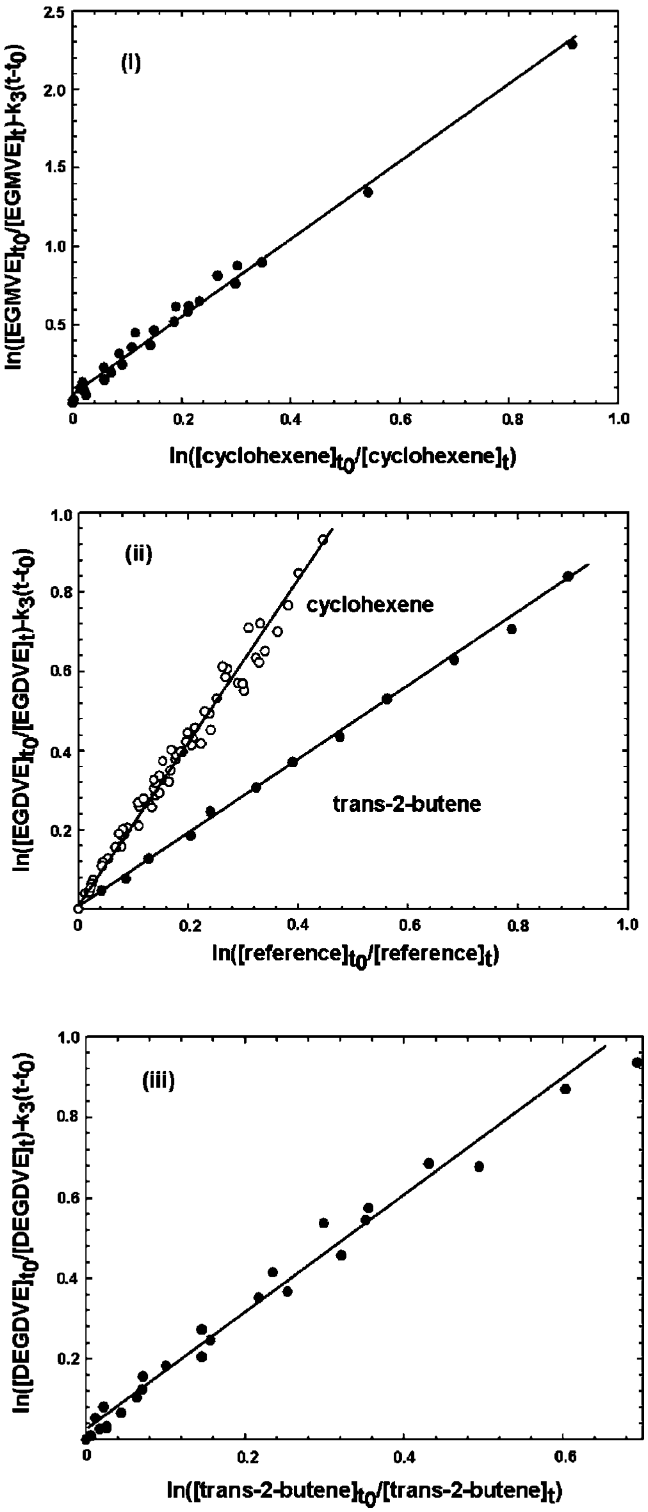


Figure 4. Plots of the kinetic data according to eq I for the gas-phase reaction of O_3 with (i) EGMVE, (ii) EGDVE, and (iii) DEGDVE.

$k_2(NO_3 + \text{isoprene}) = 6.78 \times 10^{-13}$, $k_2(NO_3 + \text{2,3-dimethyl-1,3-butadiene}) = 2.1 \times 10^{-12}$, and $k_2(NO_3 + \text{1,3-cycloheptadiene}) = 6.5 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (the recommended rate coefficients for NO_3 + isoprene and 2,3-dimethyl-1,3-butadiene are associated with an uncertainty factor of 2, and the rate for 1,3-cycloheptadiene is a single determination (give no error limits))[14] leads to the rate coefficients k_1 for the reaction of NO_3 with EGMVE, EGDVE, and DEGDVE listed in Table 3.

For the reaction of NO_3 with EGMVE, the value of $k_1(NO_3 + \text{EGMVE}) = (2.23 \pm 0.46) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} has been obtained at 298 K using a single reference compound. For the reactions of NO_3 with EGDVE and DEGDVE, there was good agreement between the values obtained with two reference compounds, and we therefore prefer to quote rate coefficients for these reactions that are averages of both determinations, that is, $k_1(NO_3 + \text{EGDVE}) = (1.96 \pm 0.50) \times 10^{-12}$ and $k_1(NO_3 + \text{DEGDVE}) = (6.14 \pm 1.38) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The quoted errors for k_1 are the standard deviations 2σ plus an additional 20% to cover uncertainties in the values of the reference rate coefficients.

It is surprising that the rate coefficient for the reaction of NO_3 with EGDVE is somewhat lower than that of NO_3 with EGMVE (see Table 3). It was expected that this reaction would be faster than NO_3 with EGMVE because EGDVE contains two double bonds in its structure. At present, we have no satisfactory explanation for this behavior, as attack of NO_3 at the double bonds in EGDVE may possibly be sterically hindered. The rate coefficient determined for DEGDVE is, however, higher than that measured for EGDVE by a factor of about 3. Here again, the reason for this is currently unclear, and steric properties might again be playing a role. Because of the extra $-OCH_2CH_2-$ unit in DEGDVE as compared to EGDVE, the double bonds in DEGDVE are probably less sterically hindered and much more open to attack by NO_3 than those in EGDVE. This is, however, pure speculation. Because there are no other reports of rate coefficients for the reactions of NO_3 with EGVEs available in the literature with which to compare the results obtained in this study, other measurements are necessary to confirm the rate data presented here before explanations are sought for the rate anomalies observed in this work. The rate coefficients for NO_3 with EGMVE and EGDVE are very similar in magnitude to those reported for the reactions of NO_3 with alkyl vinyl ethers,[26,29,32] which is what would be expected, at least for the reaction of NO_3 with EGMVE.

In the experiments on the reactions of NO_3 with EGDVE and DEGDVE, the baselines of the FTIR spectra from 2000 to 4000 cm^{-1} were elevated after introduction of N_2O_5. Figure 3 gives an example of the IR baseline elevation observed in the reaction of NO_3 with EGDVE. This elevation is possibly due to the formation of secondary organic aerosols causing scattering of the IR probing beam from the FTIR spectrometer. This elevated baseline did not affect the kinetic analyses because these were performed at wavenumbers below 2000 cm^{-1} where the baseline was not affected.

Oh and Andino[40] have reported an enhancement in the rate of reaction of OH radicals with methanol, ethanol, and 1-propanol in the presence of aerosol in the system. In the presence and absence of 500−8000 μg/m^3 of NaCl, Na_2SO_4, or NH_4NO_3 aerosol, Sørensen et al.[41] studied the effect of aerosol on the reactivity of the OH radical toward methanol, ethanol, and phenol. In contrast to the findings of Oh and Andino,[40] Sørensen et al. found that there was no discernible effect of aerosol on the rate of loss of the organics via OH radical reactions. A theoretical calculation using gas-kinetic theory indicates that under the experimental conditions applied by Oh and Andino,[40] OH radicals were at least a factor of 1000−9000 times more likely to react in the gas phase than to collide with the aerosol surface.[41] Therefore, reaction on the aerosol surface would appear to be a negligible loss process.

Because the reactions of NO_3 with the EGVEs are fast, we contend that this is also the case for the present work. On the basis of the kinetic data plots shown in Figure 2, we offer an

TABLE 4: References Employed, Measured Rate Coefficient Ratios, k_1/k_2, and Rate Coefficients k_1 (in cm^3 molecule^{-1} s^{-1}) Obtained in the Present Work at 298 K for the Reactions of O_3 with EGMVE, EGDVE, and DEGDVE Using the Relative Kinetic Technique

EGVEs	reference	k_1/k_2	$k_1 \times 10^{16}$	average $k_1 \times 10^{16}$
EGMVE $HOCH_2CH_2OCH{=}CH_2$	cyclohexene	2.49 ± 0.10	2.02 ± 0.41	2.02 ± 0.41
EGDVE $H_2C{=}CHOCH_2CH_2OCH{=}CH_2$	cyclohexene	2.01 ± 0.06	1.63 ± 0.33	1.69 ± 0.41
	trans-2-butene	0.92 ± 0.02	1.75 ± 0.35	
DEGDVE $H_2C{=}CHOCH_2CH_2OCH_2CH_2OCH{=}CH_2$	*trans*-2-butene	1.42 ± 0.07	2.70 ± 0.56	2.70 ± 0.56

TABLE 5: Estimated Atmospheric Lifetime (in hours) of EGMVE, EGDVE, and DEGDVE with Respect to Degradation by OH and NO_3 Radicals and Ozone[a]

EGVEs	τ_{OH}	τ_{NO3}	τ_{O3}
EGMVE $HOCH_2CH_2OCH{=}CH_2$	1.67	0.25	1.96
EGDVE $H_2C{=}CHOCH_2CH_2OCH{=}CH_2$	1.41	0.28	2.35
DEGDVE $H_2C{=}CHOCH_2CH_2OCH_2CH_2OCH{=}CH_2$	1.22	0.09	1.47

[a] Based on the average tropospheric concentrations of OH and NO_3 radicals and O_3 of ca. 1.6×10^6 (12 h daytime average),[42] 5.0×10^8 (12 h nighttime average),[43] and 7.0×10^{11} molecule cm^{-3} (24 h average concentration),[10−15] respectively.

additional argument to support that the formation of aerosol does not enhance the rate coefficients measured here for the reactions of NO_3 radicals with the EGVEs. When the reactions are initiated, semivolatile products are generated. The semivolatile products are likely to be low vapor multifunctional organic nitrates, which are known to be formed in the reactions of NO_3 radicals with alkenes.[12] These types of products will not be formed in the OH radical and O_3 reactions and is the probable explanation why formation of aerosol was not a problem in the kinetic investigations with these reactants. After these products have reached their saturation vapor pressure, they start to nucleate homogeneously and aerosol is formed. If the aerosol formed enhances the loss of EGDVE and DEGDVE, this would result in a faster decay of both compounds as the reaction proceeds as compared to the initial stages of the reaction. This sort of behavior would result in curvature in the types of plots (Figure 2) used to analyze the EGDVE and DEGDVE kinetic data. However, as is evident in Figure 2, this was not the case for the measurements with both EGDVE and DEGDVE, where all of the plotted data show good linearity.

O_3 Reaction. Figure 4 shows examples of the kinetic data plotted according to eq I for the reactions of ozone with all three EGVEs. In all cases, good linear plots were obtained. Corrections to the kinetic data for dark wall loss and dark decomposition of the EGVEs were of the order of approximately 35% for EGMVE and 10−15% for both EGDVE and DEGDVE. The reference hydrocarbons employed and the rate coefficient ratios, k_1/k_2, obtained from plots of the data as illustrated in Figure 4 are listed in Table 4. Using these ratios in combination with $k_2(O_3 + \text{cyclohexene}) = (8.1 \pm 2.0) \times 10^{-17}$ and $k_2(O_3 + trans\text{-2-butene}) = (1.9 \pm 0.7) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} as recommended with the given uncertainties by Calvert et al.[12] leads to the rate coefficients for the reaction of O_3 with EGMVE, EGDVE, and DEGDVE listed in Table 4. For the reactions of O_3 with EGMVE and DEGDVE, values of $k_1(O_3 + \text{EGMVE}) = (2.02 \pm 0.41) \times 10^{-16}$ and $k_1(O_3 + \text{DEGDVE}) = (2.70 \pm 0.56) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} have been obtained at 298 K using a single reference compound. For the reaction of O_3 with EGDVE, there was good agreement between the values obtained with two reference compounds, and we therefore prefer to quote a rate coefficient for the reaction that is an average of both determinations, that is, $k_1(O_3 + \text{EGDVE}) = (1.69 \pm 0.41) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}. The quoted errors of k_1 are again the standard deviations 2σ plus an additional 20% to cover uncertainties in the values of the reference rate coefficients.

As was observed for the analogue NO_3 reactions, the rate coefficient for the reaction of O_3 with EGDVE is somewhat lower than that of O_3 with EGMVE, and the rate coefficient for the reaction of O_3 with DEGDVE is higher than that of O_3 with EGDVE. As argued for the NO_3 reactions, steric factors might be playing a role in deciding the reactivity toward O_3; however, in the case of the O_3 reactions, all three rate coefficients agree within the combined error limits.

No other kinetic data are available in the literature for the reactions of O_3 with the EGVEs with which to compare the rate coefficients presented here. As for the OH radical reactions, rate coefficients for the reactions of O_3 with the EGVEs have been estimated using the AOPWIN program.[35] The program predicts rate coefficients of 0.86×10^{-17}, 1.75×10^{-17}, and 1.75×10^{-17} cm^3 molecule^{-1} s^{-1} for the reactions of OH with EGMVE, EGDVE, and DEGDVE, respectively. As for the OH radical reactions, the predicted values are all lower than the measured values. However, in contrast to the OH radical reactions, the disagreement between measured and estimated rate coefficient for the O_3 reactions is around 1 order of magnitude, showing that the SAR in the AOPWIN program needs modification to better predict rate coefficients for the reactions of O_3 with oxygenated compounds containing the vinyl ether entity.

The O_3 rate coefficients for the EGVEs are very similar in magnitude to those reported in the literature for the reactions of O_3 with alkyl vinyl ethers ($2-3 \times 10^{-16}$ cm^3 molecule^{-1} s^{-1}),[26,28,31] which is to be expected, at least for EGMVE.

The rate coefficients for the reactions of O_3 with the dienes EGDVE and DEGDVE are generally much higher than the rate coefficients reported in the literature for nonoxygenated dienes.[14] This can be attributed to the strong electron-donating effect of the $-OCH_2CH_2O-$ group to the neighboring carbon−carbon double bond, which activates it toward electrophilic addition of O_3.

Atmospheric Implications. The EGVEs atmospheric lifetimes with respect to different oxidants given in Table 5 were calculated using average tropospheric concentrations of OH and NO_3 radicals and ozone of ca. 1.6×10^6 (12 h daytime average[42]), 5.0×10^8 (12 h nighttime average[43]), and 7.0×10^{11} (24 h average concentration[10−15]) molecule cm^{-3}, respectively, and serve to illustrate the relative importance of the atmospheric degradation processes. As was found for alkyl vinyl ethers,[26] the lifetimes of EGVEs with respect to reactions with OH, NO_3, and O_3 range from a few minutes for the reactions with NO_3 radicals to a few hours for the reactions OH and O_3. The short lifetimes of the EGVEs show that they will be quickly degradated when emitted to the atmosphere and will only be actively involved in tropospheric chemistry on local to regional scales. Alcohols and ethers do not absorb UV light in the environmentally significant range (>290 nm); therefore, loss via photolysis will be a negligible loss process for this class of organic compound in the troposphere. This is supported by the tests mentioned in Experimental Methods where photolysis of the EGVEs was not observed using both visible fluorescence and UV lamps. Alcohols and ethers are generally resistant to hydrolysis. If physical removal of the EGVEs from air by precipitation and dissolution in clouds is occurring, it will only be of very limited importance because of the very short atmospheric residence times of the EGVEs due to their reactions with OH, NO_3, and O_3.

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