



Rate constants for the gas phase reactions of OH and NO₃ radicals and O₃ with selected Ethyleneglycol vinyl ethers

Sh. Zhou (1,2)*, I. Barnes (2), T. Zhu (1) and Th. Benter (2)

(1) College of Environmental Sciences, Peking University, Beijing, China

(2) FB C-Physikalische Chemie, Bergische Universitaet Wuppertal, Wuppertal, Germany

* Current Address: Department of Chemistry and Environmental Research Institute, University College Cork, Cork, Ireland

s.zhou@uucc.ie



Introduction

Vinyl ethers (ROCH=CH₂) are a class of compound released to the atmosphere entirely from anthropogenic sources. These ethers find wide application in industry as oxygenated solvents, additives and in different types of coatings. To date studies on the atmospheric chemistry of vinyl ethers have been fairly limited (1-4).

As part of systematic research work in this laboratory (5,6), we report here the first-time determinations of the rate coefficients for the reactions of OH and NO₃ radical and ozone with three ethyleneglycol vinyl ethers (EGVEs) i.e. ethyleneglycol monovinyl ether (EGMVE, HOCH₂CH₂OCH=CH₂), ethyleneglycol divinyl ether (EGDVE, H₂C=CHO-CH₂CH₂OCH=CH₂) and diethyleneglycol divinyl ether (DEGDVE, H₂C=CHOCH₂CH₂OCH₂CH₂OCH=CH₂).

Results and Discussion

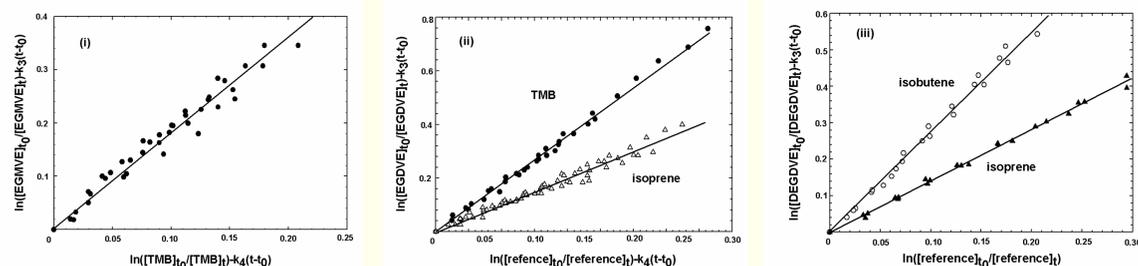


Figure 1. Plots of the kinetic data according to eq (1) for the gas phase reactions of OH radicals with EGMVE (i), EGDVE (ii) and DEGDVE (iii)

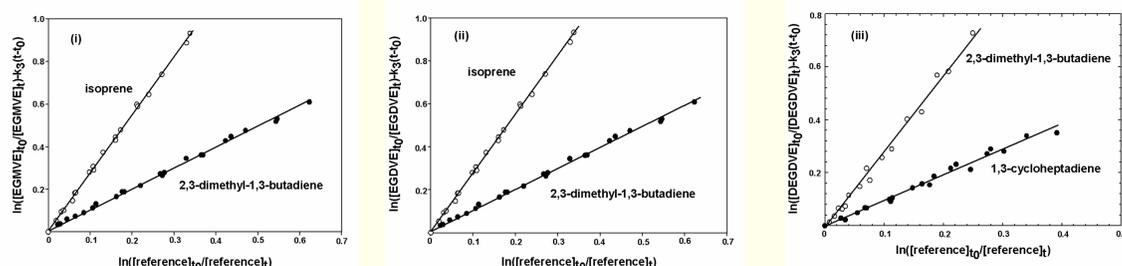


Figure 2. Plots of the kinetic data according to eq (1) for the gas phase reactions of NO₃ radicals with EGMVE (i), EGDVE (ii) and DEGDVE (iii)

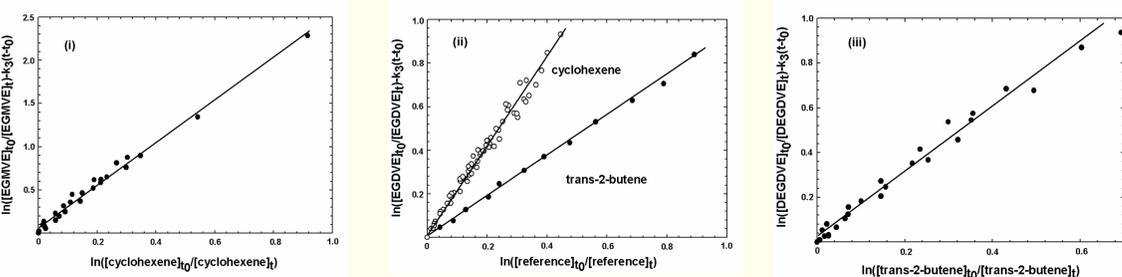


Figure 3. Plots of the kinetic data according to eq (1) for the gas phase reactions of O₃ radicals with EGMVE (i), EGDVE (ii) and DEGDVE (iii)

O₃ reaction:

Table 3. Measured rate coefficient ratios and rate coefficients for the reactions of O₃ with EGVEs obtained in the present work at 298 K

EGVEs	Reference	k ₁ /k ₂	k ₁ × 10 ¹⁶	Average k ₁ × 10 ¹⁶
EGMVE	Cyclohexene	2.49 ± 0.10	2.02 ± 0.41	2.02 ± 0.41
EGDVE	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	Trans-2-butene	1.42 ± 0.07	2.70 ± 0.56	2.70 ± 0.56

As was observed for the analogue NO₃ reactions the rate coefficient for the reaction of O₃ with EGDVE is somewhat lower than that of O₃ with EGMVE, but agrees with that of O₃ with EGMVE within the experimental error limits (Table 3).

As for the NO₃ reactions, there are no other kinetic data available in the literature for the reactions of O₃ with structurally similar alkenes and oxygenated organic compounds. A detailed comparison is thus not possible. However, the rate coefficients (in 10¹⁷ cm³ molecule⁻¹ s⁻¹) of 1.45 and 1.4 (9) reported for the reactions of O₃ with 1,4-pentadiene and 2,5-dimethyl-1,4-hexadiene, respectively, demonstrate that electron donating groups neighboring the double bond strongly activate the double bond toward electrophilic addition of O₃.

Table 4. Estimated atmospheric lifetime (in hours) of EGMVE, EGDVE and DEGDVE with respect to degradation by OH radicals ^{a)}, ozone ^{b)} and NO₃ radicals ^{c)}

EGVEs	τ _{OH}	τ _{NO₃}	τ _{O₃}
EGMVE	1.67	0.28	1.96
EGDVE	1.41	0.25	2.35
DEGDVE	1.22	0.09	1.47

^{a)} Based on the average tropospheric concentrations of OH and NO₃ radicals and O₃ of ca. 1.6 × 10⁶ (12-h daytime average) (10), 7 × 10¹¹ (24-hr average concentration) (11) and 5.0 × 10⁸ molecule cm⁻³ (12-h nighttime average) (12), respectively.

As for alkyl vinyl ethers (5), the lifetimes of the EGVEs with respect to reactions with OH, NO₃ and O₃ range from few minutes for the reactions with NO₃ radicals to a few hours for the OH and O₃ reactions.

The short lifetimes of the EGVEs show that they will be quickly degraded when emitted to the atmosphere and will only be actively involved in tropospheric chemistry on local to regional scales.

The photolysis of EGVEs is a negligible loss process for this class of organic compound in the troposphere (3).

Acknowledgement

Financial support of this work by the European Commission within the project MOST (contract EVK2-CT-2001-00114) and EUROCHAMP is gratefully appreciated.

Experimental Setup

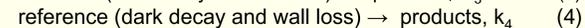
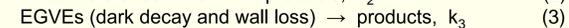
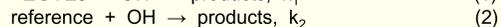
All of the experiments were performed in a 405 liter evacuable borosilicate glass chamber at (750 ± 20) Torr total pressure of synthetic air and (298 ± 3) K.

A White type mirror system coupled to an FTIR spectrometer enabled *in situ* infrared monitoring of both reactants and products.

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.

The photolysis of H₂O₂ and/or methyl nitrite (CH₃ONO) was used as the OH radical source; NO₃ radicals were produced by the thermal dissociation of N₂O₅ prepared in solid form according to a literature method (5); ozone was generated as a mixture in O₂ by passing O₂ through an electrical discharge. Ozonolysis experiments were conducted in the presence of an OH tracer scavenger (cyclohexane).

A relative kinetic technique was used to determine the rate coefficients for the reactions of OH and NO₃ radicals and O₃ with EGMVE, EGDVE and DEGDVE, e.g. for an OH radical reaction:



$$\ln \left\{ \frac{[\text{EGVEs}]_0}{[\text{EGVEs}]_t} \right\} - k_3(t-t_0) = \frac{k_1}{k_2} \times \left(\ln \left\{ \frac{[\text{reference}]_0}{[\text{reference}]_t} \right\} - k_4(t-t_0) \right) \quad (1)$$

OH radical reaction:

Table 1-1. Measured rate coefficient ratios and rate coefficients (in cm³ molecule⁻¹ s⁻¹) for the reactions of OH with EGVEs obtained in the present work at 298 K

EGVEs	OH source	Reference	k ₁ /k ₂	k ₁ × 10 ¹⁰	Average k ₁ × 10 ¹⁰
EGMVE	H ₂ O ₂	TMB ^{a)}	1.83 ± 0.05	1.04 ± 0.22	1.04 ± 0.22
EGDVE	H ₂ O ₂	TMB ^{a)}	2.28 ± 0.05	1.29 ± 0.27	1.27 ± 0.33
		Isoprene	1.24 ± 0.05	1.25 ± 0.26	
DEGDVE	CH ₃ ONO	Isobutene	2.78 ± 0.10	1.43 ± 0.29	1.42 ± 0.30
	+ NO	Isoprene	1.41 ± 0.04	1.42 ± 0.29	

^{a)} TMB-1,3,5-trimethylbenzene

Table 1-2. Comparison of the rate coefficients (in cm³ molecule⁻¹ s⁻¹) for OH + EGVEs with values reported in the literature for unsaturated organic compounds and that for OH abstraction from alkyl group in EGVEs

EGVEs (k × 10 ¹⁰)	Unsaturated organics (k × 10 ¹¹)	H-atom abstraction rate (k × 10 ¹¹) ^{a)}
EGMVE 1.04	3-Buten-1-ol HOCH ₂ CH ₂ CH=CH ₂	5.5 ^{a)}
EGDVE 1.27	1,5-Hexadiene CH ₂ =CHCH ₂ CH ₂ - CH=CH ₂	6.2 ^{b)}
DEGDVE 1.42		DEGDVE 3.9

^{a)} Reference 7; ^{b)} Reference 8; ^{c)} Estimated from SAR given in Mellouki *et al.* (2)

Good linear relationships were found for all three EGVEs and there is good agreement between the values obtained using the two different reference compounds for EGDVE and DEGDVE (Figure 1).

The rate coefficient for the reaction of OH with EGDVE is higher than that of OH with EGMVE, which is to be expected since EGDVE contains two carbon-carbon double bonds (Table 1-1). 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 cm³ molecule⁻¹ s⁻¹; this difference is much less than what one would predict using SAR for the addition of a second double bond entity.

Interestingly, the rate coefficient for DEGDVE is also higher than that of EGDVE by 1.9 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹ (Table 1-2) which is almost the calculated difference in the H-atom abstraction contributions for DEGDVE and EGDVE caused by the additional -CH₂CH₂- group.

The rate coefficients for the reactions of OH with EGMVE, and EGDVE are significantly higher than structurally similar unsaturated oxygenates 3-buten-1-ol and 1,5-hexadiene, respectively (Table 1-2). This demonstrates that the ether group neighboring the double bond activates it toward OH radical reaction. Such activation effects have also been observed for alkyl vinyl ethers (5).

NO₃ radical reaction:

Table 2. Measured rate coefficient ratios and rate coefficients for the reactions of NO₃ with EGVEs obtained in the present work at 298 K

EGVEs	Reference	k ₁ /k ₂	k ₁ × 10 ¹²	Average k ₁ × 10 ¹²
EGMVE	2,3-Dimethyl-1,3-butadiene	1.06 ± 0.05	2.23 ± 0.46	2.23 ± 0.46
EGDVE	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	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	

For all three EGVEs good linear relationships were obtained using both references (Figure 2).

It is surprising that the rate coefficient for the reaction of NO₃ with EGDVE is somewhat lower than that of EGMVE (Table 2); the rate coefficients, however, agree within the experimental error limits.

It was expected that the rate of the reaction of NO₃ with EGDVE would be faster than that with EGMVE since the former contains two double bonds in its structure. The reason for this is currently unclear.

Literature:

- Grosjean, E.; Grosjean, D. *J. Atmos. Chem.* **1999**, *32*, 205.
- Mellouki, A.; Le Bras, G.; Sidebottom, H. *Chem. Rev.* **2003**, *103*, 5077.
- Barnes, I.; Zhou, Sh.; Klotz, B. In *Final reports of the EU project MOST*; contract EVK2-CT-2001-00114; European Union: Brussels, August **2005**.
- Grosjean, D.; Williams II, E.L. *Atmos. Environ.* **1992**, *26A*, 1395.
- Zhou, Sh.; Barnes, I.; Zhu, T.; Bejan, I.; Benter, Th. *J. Phys. Chem.* **2006**, *110*, 7386.
- Zhou, Sh.; Barnes, I.; Zhu, T.; Klotz, B.; Albu, M.; Bejan, I.; Benter, Th. *Environ. Sci. Technol.* **2006**, *40*, 5415.
- Imamura, T.; Iida, Y.; Obi, K.; Nagatani, I. *et al. Int. J. Chem. Kinet.* **2004**, *36*, 379.
- Al Mulla, I.A.S. Ph.D. thesis, The National University of Ireland, **2006**
- Atkinson, R.; Arey, J. *Chem. Rev.* **2003**, *103*, 4605.
- Prinn, R.G.; Weiss, R. F.; Miller, B. R. *et al. Science* **1995**, *269*, 187.
- Platt, U.; Heintz, F. *Israel J. Chem.* **1994**, *34*, 289
- Logan, J. A. *J. Geophys. Res.* **1985**, *90*, 10463.