OH and O_3-initiated oxidation of ethyl vinyl ether

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The reaction rate constants of OH and O_3 with ethyl vinyl ether (EVE, $C_2H_5OCH=CH_2$) have been measured in the temperature range 230–372 K and 298 K, respectively. The temperature dependent rate constant for the reaction with OH was found to be well represented by the expression: $k_1 = (1.55 \pm 0.25) \times 10^{-11}$ $\exp[(445 \pm 13)/T]$ cm^3 molecule^{-1} s^{-1}, and at 298 K, $k_1 = (6.8 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The reaction rate constant of O_3 with EVE was determined to be $k_2 = (2.0 \pm 0.2) \times 10^{-16}$ cm^3 molecule^{-1} s^{-1} at 298 K. Using two different simulation chambers, the OH and O_3-initiated oxidation of ethyl vinyl ether in air was also investigated. The main products observed from both reactions were formaldehyde and ethyl formate. The results obtained are presented and their atmospheric relevance briefly discussed.

1. Introduction

Vinyl ethers are used industrially, particularly as solvents, as motor oil additives and for coatings [see *e.g.* ref. 1]. They are released into the atmosphere where they are available for photochemical transformation. The atmospheric oxidation of these oxygenated compounds can contribute to the formation of ozone and other secondary pollutants. In the troposphere, these unsaturated compounds react with OH and NO_3 radicals and with O_3. To date, a limited number of studies have been performed on this type of unsaturated ether.[2–5] Therefore, kinetic and mechanistic data are needed in order to determine their lifetime in the troposphere and to assess their contribution to urban and regional pollution.

We have studied the O_3 and OH-initiated degradation of EVE. The rate constants of its reactions with OH and O_3 have been measured over the temperature range 230–372 K and at 298 K, respectively:

$$OH + C_2H_5OCH=CH_2 \rightarrow products \qquad k_1$$
$$O_3 + C_2H_5OCH=CH_2 \rightarrow products \qquad k_2$$
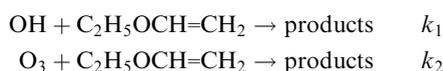
In addition, the OH and O_3-initiated oxidation mechanisms of EVE have been investigated using two different photoreactors. The data obtained are presented and discussed.

2. Experimental

The rate constant for the reaction of $C_2H_5OCH=CH_2$ with OH radicals has been measured using both an absolute method, pulsed laser photolysis-laser induced fluorescence (PLP-LIF), and a relative rate method by means of a laboratory Teflon bag. The rate constant of the reaction of the ether with O_3 has been measured using the EUPHORE photoreactor. The oxidation mechanism studies were carried using two complementary photoreactors (EUPHORE and laboratory Teflon bag).

(i) OH rate constant measurements

Absolute measurements. The PLP-LIF apparatus and procedure used to measure the OH rate constant have been described in previous publications from this laboratory [*e.g.* ref. 6], therefore, only a brief summary is presented here. OH radicals were produced by photolysis of H_2O_2 at 248 nm (KrF excimer laser). Their concentration was monitored at various reaction times ranging typically from 10 μs to 5 ms by pulsed LIF. A Nd:YAG-pumped frequency-doubled dye laser was used to excite the OH radicals at $\lambda \approx 282$ nm. Fluorescence from the OH radicals was detected by a photomultiplier fitted with a 309 nm narrow band-pass filter and the integrated signals from 10 to 15 delay times from 100 probe laser shots were averaged to generate OH concentration-time profiles over at least three lifetimes.

H_2O_2 was introduced into the reaction cell by passing a small flow of helium through a glass bubbler containing H_2O_2 solution. EVE was premixed with helium in a 10 L glass bulb to form 0.5–1% mixture at a total pressure of about 850 Torr. The gas mixture, the photolytic precursor (H_2O_2), and the bath gas (helium) flowed through the cell with a linear velocity ranging from 3 to 10 cm s^{-1}. The mixtures of EVE and H_2O_2 in helium were flowed slowly through the cell, so that each photolysis/probe sequence interrogates a fresh gas mixture and reaction products do not build up in the cell. The concentrations of the reactants were calculated from their mass flow rates, temperature, and pressure in the reaction cell. All flow rates were measured with mass flow meters calibrated by measuring the rate of pressure increase in a known volume. The pressure in the cell was measured with a capacitance manometer connected at the entrance of the cell.

Relative measurements. The experimental set-up used to measure the relative rate constant consisted of a 100 L Teflon bag and lamps positioned in a wooden box with the internal faces covered with aluminium foil. Measured amounts of reagents were flushed from calibrated bulbs into the Teflon bag through a stream of ultrapure air. The photoreactor was then filled to its full capacity at atmospheric pressure with ultrapure air. Photolysis of H_2O_2 was used as the source of OH radicals. The reactants were monitored using gas chromatography with a flame ionisation detector (GC-FID). Chromatographic separation was achieved by using a DB-1 capillary column (J&W Scientific, 30 m, 0.25 mm id, 5 μm film) maintained at 308 K. Helium was used as the carrier gas.

(ii) O_3 rate constant measurements

The outdoor European Photo-Reactor (EUPHORE) facility located in Valencia, Spain was used. EUPHORE is composed of two half spherical chambers each of 200 m^3 volume. They are made of 0.13 mm thick FPE foil with more than 80% light transmission in the UV-Visible region (280–640) nm. Purified air and reactants were introduced into the chambers *via* ports located on the floor and homogeneous gas mixtures were obtained by the use of powerful mixing fans. The chambers differ in the analytical instruments connected to each of them and in the optical path-length for the *in situ* FTIR analysis (326.8 or 553 m). Additional analysis of the reactants and products was provided by NO_x, O_3 and CO analysers, gas chromatography, HPLC and GC-MS. Details on this facility can be found elsewhere [*e.g.* ref. 7 and 8]. The chamber used for this study is the one equipped with 326.8 m optical path-length for *in situ* FTIR measurements. The IR spectra were recorded every 5 min by co-adding 280 interferograms with a resolution of 1 cm^{-1}. EVE concentration was monitored at its absorption band centred at 3000 cm^{-1}. Ozone was measured in real time by an ozone analyzer with a detection limit of 1 ppb. Known amounts of EVE and O_3 were introduced into the chamber along with SF_6 (a stable compound used to measure the dilution rate in the photo-reactor resulting from leaks in the chamber). The rate constant of the reaction of O_3 with EVE was derived from the best fitting of the reaction time-concentration of O_3 and EVE profiles.

(iii) OH-initiated oxidation mechanism study

Two different chambers were used, a 100 L Teflon bag surrounded by six lamps (Sylvania, G30W) with irradiation at 254 nm at LCSR-Orléans (the same as that used for the kinetic measurements described above) and at EUPHORE with sunlight irradiation. At LCSR, the reactant and its oxidation products were monitored using gas chromatography with a flame ionisation detector (GC-FID) under similar conditions as for the kinetic measurements. At EUPHORE, the two chambers were used.

(iv) O_3-initiated oxidation mechanism study

The experimental conditions were the same as for the kinetic study. From these experiments, we were able to extract the reaction rate constant of O_3 with EVE as well as the reaction products distribution.

Materials

The purity of the chemicals was as follows: He (UHP certified to > 99.9995% (Alphagaz));N_2–O_2 (80–20) was certified to > 99.995% (Alphagaz). Ethyl vinyl ether (> 99%) was from Aldrich. The 50 wt.% H_2O_2 solution, obtained from Prolabo, was concentrated by bubbling helium through the solution to remove water for several days prior to use and constantly during the course of the experiments. For the ozonolysis experiments, ozone was produced using an ozone generator.

3. Results and discussion

OH rate constant measurements

Absolute measurements. Kinetic experiments were performed under pseudo-first-order conditions with the concentration of ethyl vinyl ether in large excess over the OH concentration ($[EVE]_0 > 100 \times [OH]_0$). Typically, the initial OH concentration, $[OH]_0$, was around 2×10^{11} molecule cm^{-3}. The rate of

disappearance of the OH radical followed a simple exponential rate law:

$$[OH]_t = [OH]_0 e^{-k't}, \text{ where } k' = k_1[EVE] + k'_0$$

k_1 is the rate constant for the reaction of OH with EVE. The decay rate k' is the first-order OH disappearance rate in the presence of EVE and k_0' is the first-order rate constant for OH removal in absence of EVE (attributed to the diffusion of OH radicals out of the detection zone and to their reaction with H_2O_2). Typically, EVE and H_2O_2 concentrations were in the ranges $(1 - 35) \times 10^{13}$ and $(1.5 - 15) \times 10^{13}$ molecule cm^{-3}, respectively. k_0' and k'-k_0' were in the ranges 75–430 s^{-1} and 745–25000 s^{-1}, respectively. Experiments were conducted in the temperature and pressure ranges, 230–372 K and 30–320 Torr of helium, respectively. In all conditions, the OH decays were found to be exponential over at least three lifetimes.

The experimental conditions employed allowed us to perform all measurements with a high level of accuracy. The high $[EVE]/[OH]_0$ ratios and low OH concentrations made negligible the contribution from secondary reactions involving the products of reactions to the measured rate constants. Neither the variation of the gas flow rates through the reactor nor the change in the total pressure of the system showed measurable effects on the measured values of k_1. The contribution of the reaction of OH with photofragments of EVE was also negligible since this unsaturated ether is not photolysed at 248 nm, the wavelength used to generate OH radicals. Its absorption cross section was measured in this work at 254 nm using a pen ray Hg lamp coupled to a 100 cm long cell and was found to be $\sigma \approx 2 \times 10^{-22}$ cm^2 molecule^{-1} at 298 K. As expected, variation in the photolysis fluence (2–15 mJ cm^{-2}) had no effect on the determined rate constants. EVE was purified to better than 99% and hence loss of OH radicals by reaction with impurities in the gas mixtures is expected to be insignificant.

The obtained values of k_1 and the experimental conditions are listed in Table 1. The room temperature rate constant, taken as the average of all values obtained at 298 K is: $k_1 = (6.8 \pm 0.7) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The quoted error for k_1 includes 2σ from the least-squares analysis and the systematic error (5%, due to uncertainties in measured concentrations). The measured values of k_1 shown in Table 1 are plotted in the Arrhenius form in Fig. 1. An un-weighted least squares analysis of the ln k_1 *vs.* $1/T$ yields the following

Table 1 Reaction OH + $C_2H_5OCH{=}CH_2$ (EVE): Experimental conditions and measured rate constants

T/K	P/ Torr	$[EVE]/10^{14}$ molecule cm^{-3}	$k'-k'_0$/ s^{-1}	$(k_1 \pm 2\sigma) \times 10^{-11}$/ cm^3 molecule^{-1} s^{-1}
372	100	0.12–1.41	745–7056	5.05 ± 0.29
372	100	0.20–1.91	1052–9290	5.06 ± 0.31
348	100	0.26–1.87	1683–10708	5.73 ± 0.13
323	100	0.21–1.99	1454–12942	6.23 ± 0.17
298	285	0.76–3.37	5256–23675	6.88 ± 0.26
298	30	0.21–1.13	2031–8474	7.13 ± 0.23
298	100	0.45–3.52	3302–24602	6.98 ± 0.15
298	100	0.31–1.70	2124–12133	7.14 ± 0.49
298	100	0.20–2.21	1294–14542	6.66 ± 0.25
298	100	0.34–2.24	2220–14969	6.53 ± 0.45
298	100	0.26–2.33	1431–16466	6.84 ± 0.37
272	30	0.16–1.36	1589–11765	8.49 ± 0.23
272	320	0.32–2.25	2677–17162	7.77 ± 0.26
272	100	0.19–2.14	1706–17032	8.03 ± 0.21
272	100	0.34–2.53	2257–19430	7.64 ± 0.51
252	100	0.14–1.44	1426–12586	9.06 ± 0.34
252	100	0.35–2.75	2521–24091	8.61 ± 0.37
240	100	0.17–1.81	1665–17675	9.68 ± 0.25
233	100	0.19–2.36	2187–24850	10.78 ± 0.24
230	100	0.17–1.67	2137–18684	10.97 ± 0.19
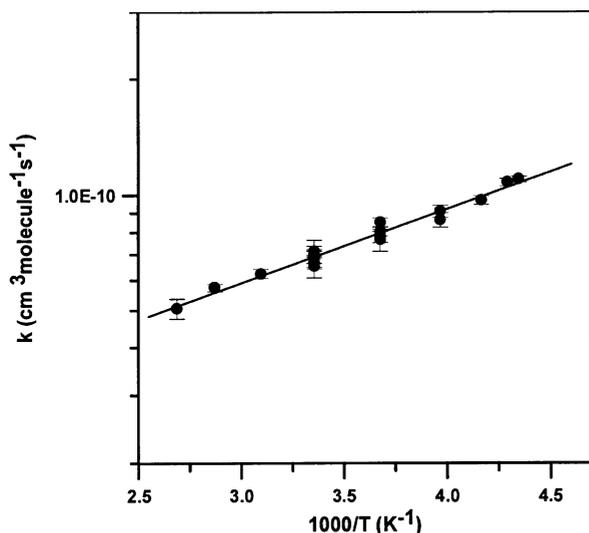
Fig. 1 Arrhenius expression of the rate constant for the reaction of OH with $C_2H_5OCH=CH_2$ in the temperature range 230–372 K. The solid line represents the Arrhenius parameter least-squares fit to the individual data points. The error bars of the individual points are 2σ and do not include estimated systematic errors.

Fig. 2 Decays of $C_2H_5OCH=CH_2$ vs. reference compounds in the presence of OH.

temperature dependent expression of k_1 in the temperature range 230–372 K: $k_1 = (1.55 \pm 0.25) \times 10^{-11} \exp[(445 \pm 13)/T]$ cm^3 molecule^{-1} s^{-1}.

Uncertainties are $2A\sigma_{\ln A}$ and $2\sigma_{E/R}$, for A and E/R, respectively. These data show a negative temperature dependence of the reaction rate constant which suggests a mechanism proceeding mainly by addition of the OH radical to the double bond of $C_2H_5OCH=CH_2$. Most experiments were conducted at around 100 Torr of helium, however, variation of the pressure in the range 20–320 Torr did not show any effect on the obtained rate constants, which in turn indicates that the high pressure limit is already reached at $P = 20$ Torr.

Relative rate measurements. Relative rate constants were measured by comparing the OH reaction rate with ethyl vinyl ether to that with reference compounds:

$$OH + EVE \rightarrow Products \qquad k_1$$
$$OH + Reference \rightarrow Products \qquad k_{ref}$$

Assuming that the compounds are only consumed by reaction with OH, it can be shown that:

$$\ln([EVE]_0/[EVE]_t) = k_1/k_{ref} \ln([ref]_0/[ref]_t)$$

where the subscripts 0 and t indicate concentrations before irradiation and at time t, respectively.

The rate constant for the reaction of OH with ethyl vinyl ether was measured at (298 ± 3) K and 760 Torr, relative to the rate constant of OH with isoprene and 2,3-dimethylbuta-1,3-diene. The initial concentrations of EVE and the references

were in the range 37–55 ppm. Photolysis of H_2O_2 at $\lambda = 254$ nm was used to generate OH radicals. The compounds showed a good stability when they were mixed in the chamber with H_2O_2 and kept in the dark for about 30 min. Moreover, in the absence of H_2O_2, the photolysis of the mixtures (EVE and reference in air) for more than 1 h did not show any decrease in the concentrations. Fig. 2 shows an example of the obtained relative loss of ethyl vinyl ether versus that of the reference compounds in the presence of OH. In Table 2, the experimental conditions and the obtained rate constant ratios are given. The rate constant of the reaction of OH with the references used in this work were taken as 1.25×10^{-10} cm^3 molecule^{-1} s^{-1} [9] for 2,3-dimethylbuta-1,3-diene and 1.01×10^{-10} cm^3 molecule^{-1} s^{-1} for isoprene.[10] While averaging the values from different experiments, we obtained: $k_1 = (7.3 \pm 0.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. The quoted error represents twice the standard deviation, to which we have added an error of 10% on the reference rate constants. This value is in good agreement with that obtained by absolute technique.

To our knowledge, this work is the first to report the reaction rate constant of OH with $C_2H_5OCH=CH_2$. The only other available rate constant of OH with a vinyl ether is that with methyl vinyl ether ($CH_3OCH=CH_2$) by Perry et al.[2] Using the flash photolysis-resonance fluorescence technique, these authors reported the following Arrhenius expression in the temperature range 299–427 K: $k = 6.1 \times 10^{-12} \exp(511/T)$ cm^3 molecule^{-1} s^{-1}, which shows a negative temperature dependence similar to that observed in this work for k_1. At 299 K, the reported value was $k = (3.35 \pm 0.34) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} which is a factor of two lower than the k_1 value. Both values are higher than those of the reaction rate constants of OH with simple ethers (e.g. $k(OH + C_2H_5OC_2H_5) = $

Table 2 Reactant concentrations and slopes k_1/k_{ref} and the obtained rate constants for the reaction of OH with ethyl vinyl ether at (298 ± 3) K

[EVE] (ppm)	Reference	[Reference] (ppm)	$(k_1/k_{ref})^a$	k_1 /cm^3 molecule^{-1} s^{-1}
37	Isoprene	37	0.69 ± 0.03	6.92×10^{-11}
55	Isoprene	55	0.70 ± 0.02	7.05×10^{-11}
46	2,3-Dimethylbuta-1,3-diene	46	0.59 ± 0.03	7.38×10^{-11}
55	2,3-Dimethyl-1,3-buta-1,3-diene	55	0.62 ± 0.02	7.76×10^{-11}
Average				$(7.3 \pm 0.9) \times 10^{-11}$

^{a} The quoted errors are twice the standard deviation arising from the least-squares fit of the data and do not include the estimated error.

1.36×10^{-11} and $k(OH + C_3H_7OC_3H_7) = 2.17 \times 10^{-11}$, in cm^3 $molecule^{-1}$ s^{-1} [6]). The reaction rate constant of OH with methyl vinyl ether from Perry *et al.* is close to that of OH with propene ($k(OH + CH_2=CHCH_3) = 2.63 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [11]), but k_1 measured in this work is two times higher than that of OH with but-1-ene ($k(OH + CH_2=CHC_2H_5) = 3.1 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1} [11]). This may indicate that C_2H_5O activates the double bond by electron donating more than CH_3O and C_2H_5.

Ozone rate constant measurement

Two experiments were performed, in the dark, with initial concentrations of O_3 and $C_2H_5OCH=CH_2$ of 205 ppb and 482 ppb in the first run and 214 ppb and 830 ppb in the second. The experiments were conducted in the presence of a large excess of cyclohexane (50 ppm) to scavenge the OH radicals which may be produced from the reaction of O_3 with EVE. The dilution rate of O_3 and EVE were obtained from the decay of SF_6 added to the reaction mixture. The disappearances of ozone and EVE were due to the reaction with each other and also to the dilution in the chamber while the disappearance of SF_6 is due only to its dilution:

$$O_3 + C_2H_5OCH=CH_2 \rightarrow products \qquad k_2$$

The dilution rate of O_3, EVE and SF_6 was obtained from the measurement of SF_6 concentration *versus* time. The dilution rate of SF_6, k_{SF6}, was measured by FTIR at its absorption band centred at 947 cm^{-1} and was found to be typically 6×10^{-6} s^{-1}.

The best fit to experimental reaction time-concentration profiles of O_3 and EVE was obtained with the values of $k_2 = 2.0 \times 10^{-16}$ and 1.9×10^{-16} cm^3 $molecule^{-1}$ s^{-1}, for the first and the second experiment, respectively. The concentration profiles and the fitting for the second experiment are shown in Fig. 3. The derived average value of the rate constant for the O_3 reaction with ethyl vinyl ether at (298 ± 3) K is: $k_2 = (2.0 \pm 0.2) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}. This value is in reasonable agreement with that reported previously by Grosjean and Grosjean[4] who obtained $k_2 = (1.54 \pm 0.30) \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1} under pseudo-first-order conditions with excess of ozone.

Compared to the rate constants of the reaction of ozone with simple alkenes, k_2 is much higher (*e.g.* propene,

$(9.6 \pm 0.4) \times 10^{-18}$, but-1-ene $(8.8 \pm 0.6) \times 10^{-18}$ cm^3 $molecule^{-1}$ s^{-1} [12]). It is also higher than that of the reaction of O_3 with other oxygenated compounds such as aldehydes and esters, reflecting the electron donating and withdrawing effects of RO and $>C=O$ groups, respectively.[4]

Mechanistic studies

(a) OH-initiated oxidation. In the 100 L photoreactor, described in the Experimental section, experiments were conducted in the presence and absence of NO. The initial concentrations of EVE and NO (when present) were in the range 60–120 ppm and 40–90 ppm, respectively. Mixtures of EVE/H_2O_2 with and without NO in air were irradiated for typically 240 min. EVE showed a good stability when the mixtures were kept in the dark for 60 min. The main oxidation product detected by GC-FID was ethyl formate ($C_2H_5OC(O)H$), both in the absence and presence of NO. Its formation yield derived from different experiments was $(92 \pm 7)\%$ and $(83 \pm 7)\%$ in the presence and absence of NO, respectively.

Two experiments were performed at EUPHORE where the initial reactant concentrations were much lower than those used in the laboratory. Both experiments were conducted in the presence of NO_x. The initial reactant concentrations were: $[EVE] = 0.65$ and 1.27 ppm, $[NO] = 86$ and 38 ppb, and $[NO_2] = 60$ and 28 ppb in the first and second run, respectively. The mixtures were exposed to natural sunlight for less than 1 h. The analysis of the reactants and products were carried out by *in situ* FTIR, GC-FID, NO_x, and O_3 analysers. An example of the obtained FTIR spectra before irradiation and after 45 min of irradiation of the mixture is given in Fig. 4. As can be seen from Fig. 5, the obtained concentration-time profiles of the ethyl vinyl ether and its oxidation products, confirm that ethyl formate is the main product of the reaction, similar to what was observed in the laboratory. Formaldehyde and CO were also detected as products. The concentration-time profiles of EVE and the products were obtained from integration of the IR spectra between 3228 and 2716 cm^{-1} for EVE, 1834 and 1690 cm^{-1} for ethyl formate, 2637 and 3079 cm^{-1} for formaldehyde, and 2020 and 2230 cm^{-1} for CO. The derived yields are $(85 \pm 10)\%$ for ethyl formate and $(70 \pm 8)\%$ for formaldehyde (Fig. 6). The carbon balance in the experiments conducted at Euphore was about 80%.

The observed products can be explained by a mechanism proceeding mainly by OH-addition to the carbon–carbon double bond:

$$C_2H_5OCH=CH_2 + OH(+O_2 + NO + M)$$
$$\rightarrow C_2H_5OCH(OH)CH_2O + NO_2 \qquad (1a)$$

$$C_2H_5OCH=CH_2 + OH(+O_2 + NO + M)$$
$$\rightarrow C_2H_5OCH(O)CH_2OH + NO_2 \qquad (1b)$$
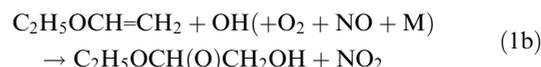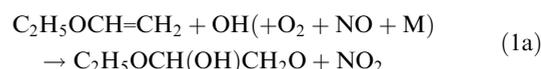
The hydroxyalcoxyl radicals $C_2H_5OCH(OH)CH_2O$ and $C_2H_5OCH(O)CH_2OH$ decompose, react with O_2, or isomerise. The reactions of these two radicals with O_2 may lead to hydroxycarbonyl compounds ($C_2H_5OCH(OH)CHO$ and $C_2H_5OC(O)CH_2OH$) while their decomposition leads to ethyl formate and formaldehyde:

$$C_2H_5OCH(OH)CH_2O(+M) \rightarrow C_2H_5OCHOH + HCHO$$
$$C_2H_5OCHOH + O_2 \rightarrow C_2H_5OC(O)H + HO_2$$

and

$$C_2H_5OCH(O)CH_2OH(+M) \rightarrow C_2H_5OC(O)H + CH_2OH$$
$$CH_2OH + O_2 \rightarrow HCHO + HO_2$$
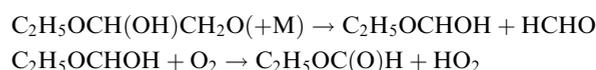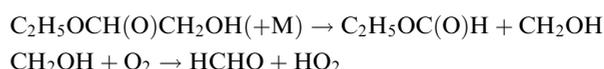
The detection of high yields of ethyl formate and formaldehyde indicates that the decomposition of the two
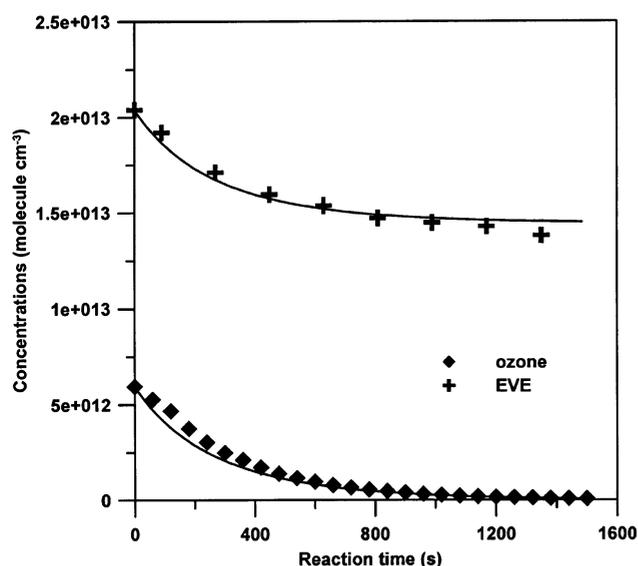
Fig. 3 Reaction of O_3 with $C_2H_5OCH=CH_2$, experimental and fitted concentration–time profiles ($[EVE]_o = 830$ ppb, $[O_3]_o = 214$ ppb).
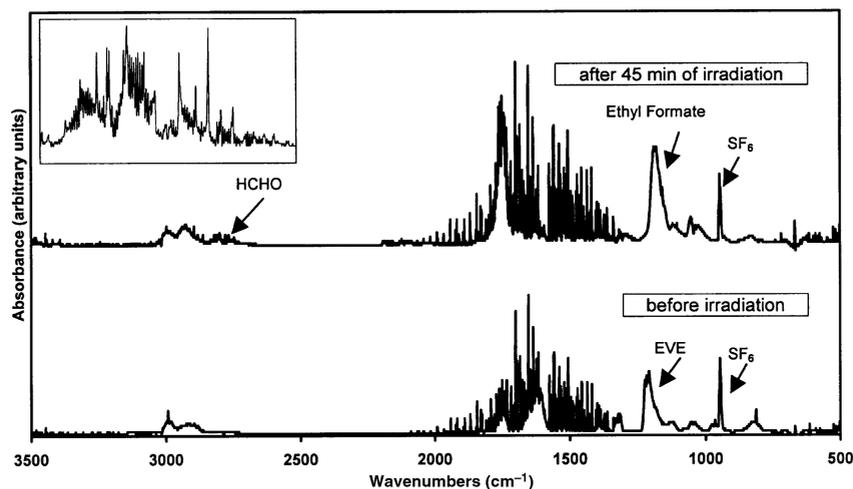
Fig. 4 OH reaction with $C_2H_5OCH=CH_2$, an example of the obtained FTIR spectra before and after 45 minutes solar irradiation of the mixture obtained at EUPHORE.

hydroxyalcoxyl radicals dominates over the other processes (reaction with O_2 and isomerisation).

The other possible mechanism is the H-atom abstraction from the C_2H_5- group which produces vinyl esters such as $CH_3C(O)OCH=CH_2$ and $HC(O)OCH=CH_2$ when the abstraction is from the $-CH_2-$group:

$$C_2H_5OCH=CH_2 + OH(+O_2 + NO + M)$$
$$\rightarrow CH_3CH(O°)OCH=CH_2 + NO_2 + H_2O$$

$$CH_3CH(O°)OCH=CH_2(+O_2) \rightarrow CH_3C(O)OCH=CH_2$$

$$CH_3CH(O°)OCH=CH_2(+M + O_2)$$
$$\rightarrow HCHO + H(O)COCH=CH_2$$
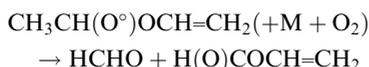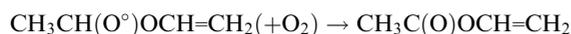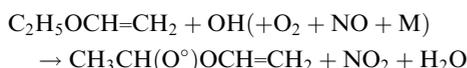
The H-abstraction from the methyl group may lead mainly to $HC(O)CH_2OCH=CH_2$:

$$C_2H_5OCH=CH_2 + OH(+O_2 + NO + M)$$
$$\rightarrow (O°)CH_2CH_2OCH=CH_2 + NO_2 + H_2O$$

$$(O°)CH_2CH_2OCH=CH_2(+O_2) \rightarrow H(O)CCH_2OCH=CH_2$$

However, none of these compounds was detected, indicating that the OH oxidation of EVE proceeds essentially by OH addition to the carbon-carbon double bond.

A few runs were carried out in the absence of NO_x in the laboratory. Here also, the main reaction product observed was ethyl formate with a formation yield of $(84 \pm 4)\%$. This can be due to the self reactions:

$$C_2H_5OCH(OH)CH_2O_2 + C_2H_5OCH(OH)CH_2O_2$$
$$\rightarrow 2C_2H_5OCH(OH)CH_2O + O_2$$
$$C_2H_5OCHO_2CH_2OH + C_2H_5OCHO_2CH_2OH$$
$$\rightarrow 2C_2H_5OCH(O)CH_2OH + O_2$$

$C_2H_5OCH(OH)CH_2O$ and $C_2H_5OCH(O)CH_2OH$ radicals decompose or react with O_2 to form ethyl formate.

It has to be mentioned that the amount of ozone formed in the Euphore experiments (ca. 200 ppb) could contribute to the consumption of EVE and then to the product formation since its reaction with EVE is fast enough. However, the formation yields of the observed products from the OH-initiated oxidation products were derived from the initial period of the experiments when the O_3 concentrations were still low.

Fig. 5 $C_2H_5OCH=CH_2$ and products concentrations *versus* reaction time in the OH-initiated oxidation of $C_2H_5OCH=CH_2$ in air in the presence of NO_x at EUPHORE.
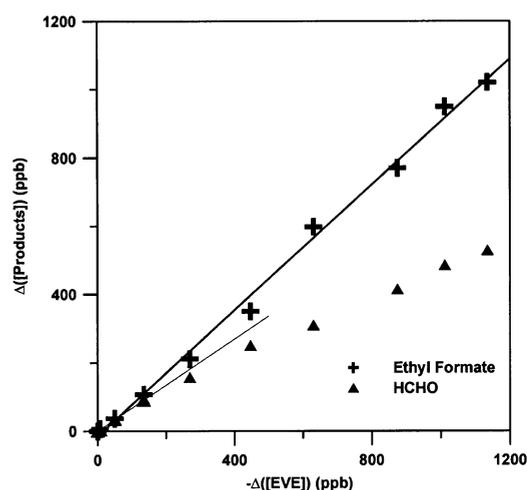
Fig. 6 Concentrations of product *versus* consumption of $C_2H_5OCH=CH_2$ in the OH-oxidation of $C_2H_5OCH=CH_2$ in air, $[C_2H_5OCH=CH_2]_0 = 1270$ ppb (the yield of HCHO was deduced from the initial period of the experiment).

(b) O$_3$-initiated oxidation. Two experiments were performed at EUPHORE under the same experimental conditions as those used in the kinetic study. The identified reaction products were ethyl formate and formaldehyde with formation yields of $(86 \pm 6)\%$ and $(21 \pm 4)\%$, respectively, in the first experiment and $(88 \pm 4)\%$ and $(17 \pm 3)\%$, in the second. An example of the obtained reaction time-concentration profiles of reactants and products is given in Fig. 7. Fig. 8 shows an example of the product formation *versus* the consumed ethyl vinyl ether. These linear profiles indicate that ethyl formate and formaldehyde are primary products of the reaction.

The reaction of O$_3$ with C$_2$H$_5$OCH=CH$_2$ proceeds by initial addition of O$_3$ to the carbon-carbon double bond, similar to that of O$_3$ with olefins, followed by decomposition of the ozonide to form formaldehyde and ethyl formate as stable compounds in addition to two criegee intermediates:

$$O_3 + C_2H_5OCH=CH_2 \rightarrow C_2H_5OC^\circ HOO^\circ + HCHO \quad (2a)$$

$$O_3 + C_2H_5OCH=CH_2 \rightarrow C_2H_5OC(O)H + HC^\circ HOO^\circ \quad (2b)$$

The energy rich criegee intermediates C$_2$H$_5$OCHOO and HCHOO may thermally stabilize, rearrange, react or decompose to form other stable compounds. However, we have not observed any other compound using FTIR and GC-FID methods besides formaldehyde and ethyl formate. The observed products and their yields, $(19 \pm 4)\%$ for formaldehyde and $(87 \pm 6)\%$ for ethyl formate, provided that the criegee intermediates do not form formaldehyde or ethyl formate, support the general mechanism of the reaction of ozone with unsaturated aliphatic oxygenates suggested by Grosjean and Grosjean:[4, 5]

$$O_3 + R_1R_2C=CR_3X \rightarrow \alpha(R_1COR_2 + R_3CXOO)$$
$$+ (1 - \alpha)(R_3C(O)X + R_1C(R_2)OO)$$
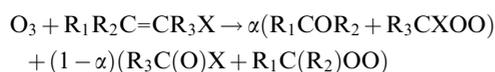
R$_1$, R$_2$, and R$_3$ = H or alkyl, X is the oxygen-containing substituent, R$_1$COR$_2$ and R$_3$C(O)X are the primary products and R$_3$CXOO and R$_1$C(R$_2$)OO are the carbonyl oxide criegee intermediates. In the case of ethyl vinyl ether, R$_1$ = R$_2$ = R$_3$ = H, and X = C$_2$H$_5$O.

The reaction of O$_3$ with C$_2$H$_5$OCH=CH$_2$ has been studied previously by Grosjean and Grosjean.[5] These authors reported the following product yields: formaldehyde $(48.7 \pm 5.2)\%$, ethyl formate $> 38.8\%$, formic acid 25.4% and cyclohexanone $(0.3 \pm 0.2)\%$. These yields are different from those obtained in this work. Grosjean and Grosjean stated that their measured yield of ethyl formate was probably a lower limit.[5] The
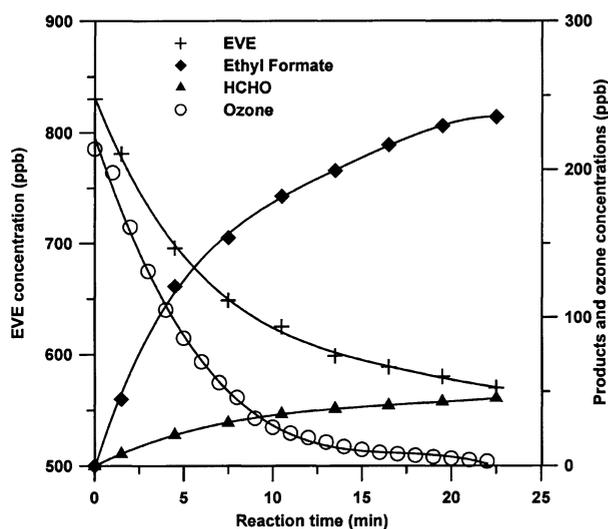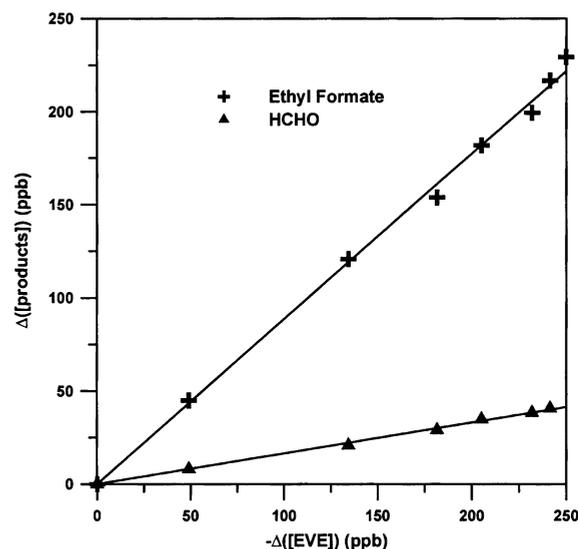
Fig. 8 Concentrations of products *versus* consumption of C$_2$H$_5$OCH=CH$_2$ in the O$_3$-initiated oxidation of C$_2$H$_5$OCH=CH$_2$ in air at EUPHORE, [C$_2$H$_5$OCH=CH$_2$]$_0$ = 830 ppb.

observed formic acid was attributed by the authors to reactions involving the criegee intermediates and the cyclohexanone to the reaction of OH with cyclohexane (added to the mixture) which is an indication of the formation of OH radicals in the ozonolysis of ethyl vinyl ether. From our own experiments, we are not able to draw conclusions on the fate of the carbonyl oxide criegee intermediates.

4. Atmospheric implications

The results obtained in this work provide some information about the atmospheric fate and impact of ethyl vinyl ether. The rate data obtained contribute to a better definition of its tropospheric lifetime. With a typical tropospheric OH concentration of 1×10^6 molecule cm^{-3} and O$_3$ concentration of 1.3×10^{12} molecule cm^{-3}, the estimated tropospheric lifetimes of EVE are respectively 4 h and 1 h. These results show that EVE will be oxidised very rapidly by reaction with OH and O$_3$ near its anthropogenic sources. OH and O$_3$-initiated oxidation will lead to the formation of the carbonyl compounds HCHO and C$_2$H$_5$OC(O)H, as reported in the present work. The rather short-lived EVE could have a local impact which, however, is not only defined by the persistence of this unsaturated ether but also by the fate of its oxidation products. HCHO will be removed by photolysis or reaction with OH and has a lifetime of less than a day while ethyl formate will be oxidised mainly by reaction with OH radicals leading to formic acid and acetic formic anhydride which are highly soluble and may be rapidly incorporated into cloud droplets.[13] C$_2$H$_5$OC(O)H has a lifetime of two weeks $(k_{OH} = 8.5 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}).[14] The formation of ethyl formate may reduce significantly the local impact of ethyl vinyl ether.

Acknowledgements

Fig. 7 Concentrations of products and reactants *versus* reaction time in the O$_3$-initiated oxidation of C$_2$H$_5$OCH=CH$_2$ in air at EUPHORE.

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