Atmospheric Oxidation Mechanisms of Unsaturated Oxygenated VOCs

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Introduction

Unsaturated oxygenated volatile organic compounds are an important class of compounds which are used in different industries. These compounds are emitted to the atmosphere where they are oxidised to produce ozone and other secondary pollutants in urban and rural areas. The main tropospheric degradation processes for this type of compounds are reactions with OH radicals, ozone and NO_3 radicals. Kinetic and mechanistic data are needed to better understand the atmospheric degradation mechanisms of these compounds and therefore to assess their impact on air quality.

In this work, we have studied the O_3 and OH-initiated degradation of Ethyl Vinyl Ether (EVE, $C_2H_5OCH{=}CH_2$) and Methyl Methacrylate (MMAC, $CH_2{=}C(CH_3)C(O)OCH_3$). The absolute rate constants for reactions of O_3 with EVE and MMAC and that of OH radicals with EVE have been measured. The oxidation mechanisms of $C_2H_5OCH{=}CH_2$ and $CH_2{=}C(CH_3)C(O)OCH_3$ initiated by OH and O_3 have been investigated in our laboratory and at EUPHORE.

Experimental and results

Kinetic studies

OH rate constant measurement :

The pulsed laser photolysis - laser induced fluorescence (PLP-LIF) technique was used to measure the rate constant of the OH + EVE reaction. OH radicals were produced by photolysis of H_2O_2 at $\lambda = 248$ nm. The OH temporal concentration profiles were obtained by pulsed laser induced fluorescence. Reactions were studied under pseudo-first order conditions with the OH concentration much lower than that of EVE ($[EVE]_o >> [OH]_o$). Under these conditions, the OH concentration time profiles followed the pseudo-first-order rate law:

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

where k is the rate coefficient for the reaction of OH with EVE. The decay rate, k'_o, is the first-order OH decay rate in the absence of the ether; it is the sum of the reaction rate of OH with its precursor (H_2O_2), and the diffusion rate of OH out of the detection zone.

Rate constants were determined over the temperature and the pressure ranges 230-372 K and 30-320 Torr, respectively. The obtained values were (in cm^3 $molecule^{-1}$ s^{-1}) $k_{298} = (6.8 \pm 0.7)x10^{-11}$ and $k_{230\text{-}372} = (1.55\pm0.25)x10^{-11}exp[(445\pm13)/T]$. The measured rate constants are shown plotted in Arrhenius form in figure 1. This latter plot shows a negative temperature dependence of the rate constant which is consistent with a mechanism proceeding mainly by addition of OH radicals to the double bond of the ether.

Ozone rate constant measurements :

Although the major application of EUPHORE is for mechanistic studies, it was also used to determine the rate constant for the reaction of ozone with EVE and MMAC. For the reaction of O_3 with EVE, the initial concentrations of ozone and EVE were 207 ppb ($5.2\text{x}10^{12}$ molecule cm^{-3}) and 485 ppb ($1.2\text{x}10^{13}$ molecule cm^{-3}), respectively. The other reaction was studied using the following initial concentrations [MMAC] = 1.37 ppm and [O_3] = 279 ppb. The reactions were studied in the presence of large excess of cyclohexane (> 50 ppm, $1.25\text{x}10^{15}$ molecule cm^{-3}) to scavenge the OH radicals which may be produced from the reaction of O_3 with EVE or MMAC. Ozone was measured in real time by an ozone analyser. The concentrations of EVE and MMAC were measured using FTIR and gas chromatography techniques.

From the fitting to the obtained concentration profiles of O_3 and the two unsaturated oxygenated VOCs we determined the rate constant values at 298 K:

$$k(O_3 + C_2H_5OCH{=}CH_2) = (2.0 \pm 0.4)\text{x}10^{-16}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

$$k(O_3 + CH_2{=}C(CH_3)C(O)OCH_3) = (8.7 \pm 0.8)\text{x}10^{-18}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}.$$

As an example of the obtained results, figure 2 shows the experimental and fitted data for the reaction of O_3 with EVE.

Product studies

O_3 reaction :

One experiment was performed for each reaction and that was at the EUPHORE facility. The initial experimental conditions were the same as those used for the kinetic studies. In the reaction of O_3 (207 ppb) with EVE (485 ppb) (in the presence of excess of cyclohexane, 50 ppm), the main products detected were ethyl formate (85 %) and formaldehyde (20 %). The profiles of the reactants and products are shown in figure 3. In the reaction of O_3 (279 ppb) with MMAC (1.37 ppm)) (in the presence of excess of cyclohexane, 57 ppm), the main products detected were methyl pyruvate, $CH_3C(O)C(O)OCH_3$ (45 %) and formaldehyde (50 %).

The observd products are the expected primary products resulting from the well established ozonolysis mechanism:

$$O_3 + R_1R_2C{=}CR_3X \rightarrow \alpha(R_1COR_2 + R_3C(X)OO) + (1\text{-}\alpha)(R_3COX + R_1C(R_2)OO)$$

For both reactions the total yields of the primary products are close to unity as expected from the above mechanism. However, for the O_3 + EVE reaction, the yields of the primary products were significantly different from previous measurements [1]: 20% compared to 49% for formaldehyde, and 85% compared to 39 % for ethyl formate. For the O_3 + MMAC reaction, there is no previous data, but the product yield compares well with previous measurements for the similar reaction of O_3 with methyl acrylate, where the following yields were obtained: formaldehyde (55%) and methyl glyoxalate (40%) [1].

OH reactions :

1/ A first series of experiments was performed, in our laboratory, at atmospheric pressure and 298 ± 3 K, in a small Teflon bag (volume ≈ 100 L) surrounded by UV lamps (254 nm). Quantitative analysis were carried out using gas chromatography FID/MS and FTIR. The experiments were performed in synthetic air, using H_2O_2 as the OH radical source, in the presence and absence of NO. The main product observed, in the presence and absence of NO, were ethyl formate ((92 ± 7) % and (83 ± 7) %, respectively) for EVE, and methyl pyruvate (≈ 67 %) for MMAC.

2/ One experiment was performed at EUPHORE for each compound. EVE (650 ppb) and NO (86 ppb) or MMAC (1.18 ppm) and NO (120 ppb) were introduced into the chamber in a stream of dry air. Figure 4 shows the concentration-time profiles measured during the photooxidation of $C_2H_5OCH{=}CH_2$. The analysis was carried out using FTIR, GC/FID/PID/ECD, NO_x, O_3, and CO analysers. The main observed products during the photooxidation of EVE were ethyl formate, formaldehyde, ozone, and CO with the following yields: ethyl formate (64 % (FID), 70 % (PID), and 79 % (FTIR)) and formaldehyde (42 % (FTIR)). The main products observed during the photooxidation of MMAC were methyl pyruvate, formaldehyde, ozone, and CO. The above reported product yields need, however, to be refined to take into account the contribution of ozonolysis which was found to become significant when sufficient ozone concentration was produced in the chamber.

Nevertheless, the obtained data, in our laboratory or at EUPHORE, show that the main products of the OH-initiated oxidation of $C_2H_5OCH{=}CH_2$ is $C_2H_5OC(O)H$ and that of $CH_2{=}C(CH_3)C(O)OCH_3$ is $CH_3C(O)C(O)OCH_3$. These results are consistent with a mechanism proceeding essentially through addition of OH radical to the double bound of the unsaturated VOCs (already mentioned in the OH kinetic section for EVE).

Atmospheric implications

Using the rate constants for the reactions of EVE and MMAC with OH (6.8×10^{-11} and 2.6×10^{-11} respectively) and with O_3 (2×10^{-16} and 8.7×10^{-18}, respectively) and the typical atmospheric concentrations of OH (10^6) and O_3 (1.3×10^{12}) molecule cm^{-3}, the calculated lifetimes of these two VOCs, with respect to their reactions with OH and O_3, are for EVE around 4 hours and 1 hour, and for MMAC around 11 hours and 25 hours, respectively. This shows that these unsaturated oxygenated VOCs will be oxidised very rapidly by reaction with OH or O_3 and that will lead to the formation of carbonyls such as HCHO, C_2H_5OCHO and $CH_3C(O)C(O)OCH_3$ as reported in the present work. The atmospheric impact of EVE and MMAC is not only defined by their persistence (determined by their oxidation rate by OH or O_3) but also by the fate of its oxidation products.

References

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J. Atmos. Chemistry, 32, 205-232, 1999

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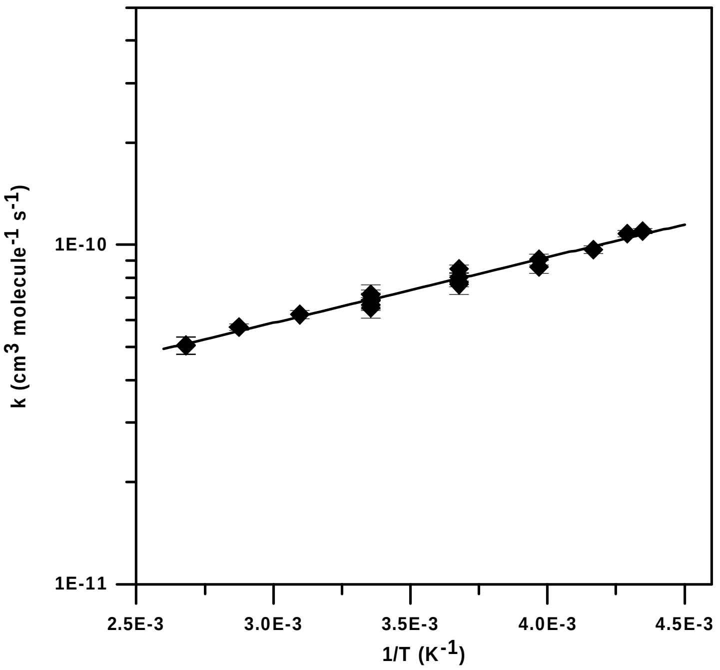

Fig. 1 : Plot of k(OH + $C_2H_5OCH=CH_2$) vs 1/T in the temperature range (230 – 372) K**.**

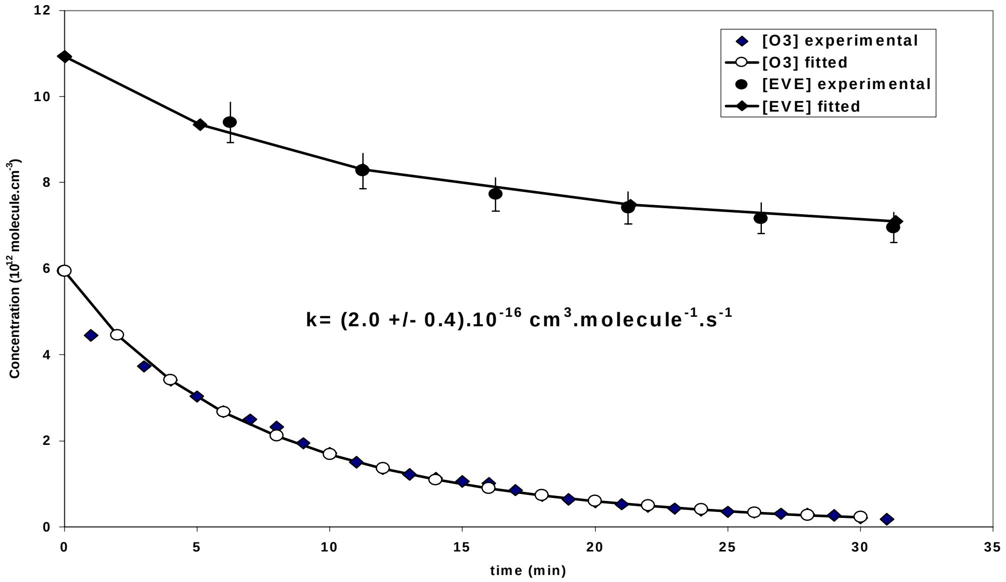

Fig. 2 : Reaction of $C_2H_5OCH=CH_2$ with O_3: Experimental (obtained at EUPHORE) and fitted concentration-time profiles ($[EVE]_o$ = 485 ppb, $[O_3]_o$ = 207 ppb).

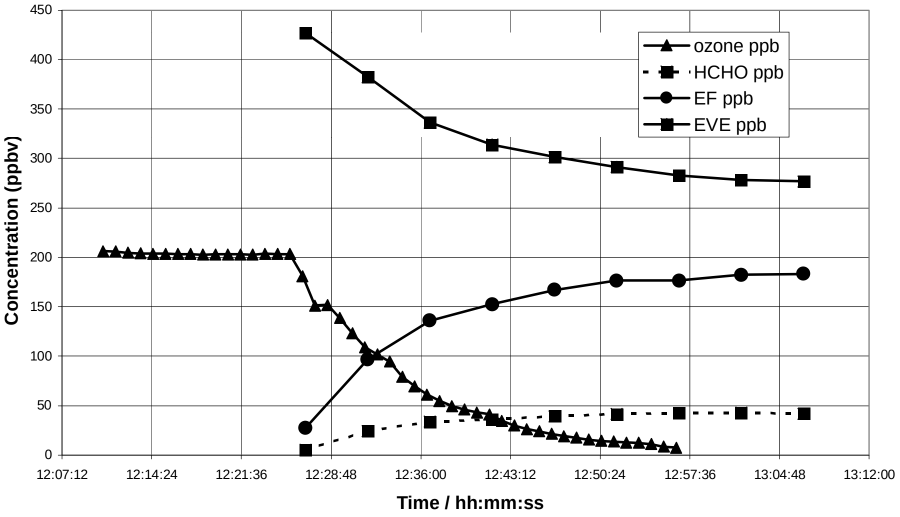

Fig. 3: Concentration-time profiles measured during ozonolysis of $C_2H_5OCH{=}CH_2$ at EUPHORE, ($[C_2H_5OCH{=}CH_2]_o$ = 485 ppb, $[O_3]_o$ = 207 ppb, $[\text{cyclohexane}]_o$ = 50 ppm).

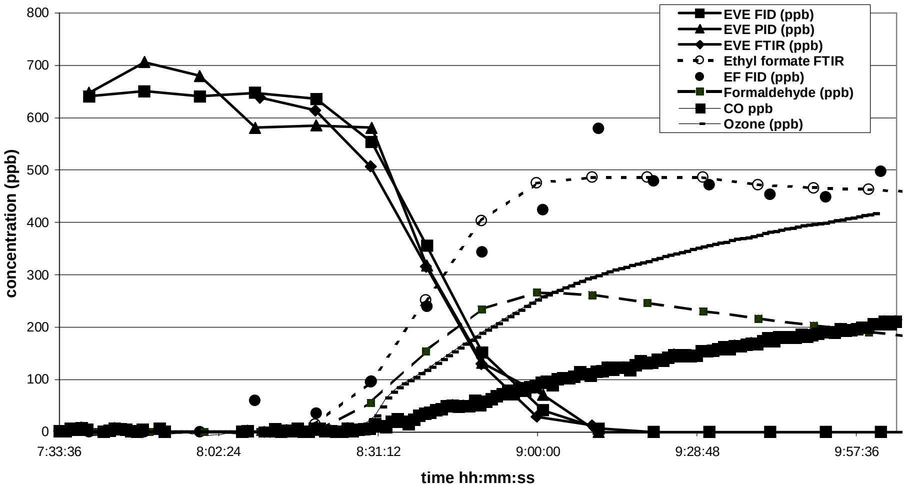

Fig. 4: Concentration-time profiles measured during the OH-initiated photooxidation of $C_2H_5OCH{=}CH_2$ at EUPHORE (15/07/99), ($[C_2H_5OCH{=}CH_2]_o$ = 650 ppb, $[NO]_o$ = 86 ppb)