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Atmospheric photodegradation of ethyl vinyl ketone and vinyl propionate initiated by OH radicals

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ABSTRACT

Rate coefficients for the reactions of hydroxyl radicals with ethyl vinyl ketone and vinyl propionate were determined at 298 K and atmospheric pressure. A collapsible chamber with gas chromatography was used to perform relative kinetic determinations. The room temperature rate coefficients (in cm³ molecule⁻¹ s⁻¹) were: $k_1(OH + CH_2 = CHC(O)CH_2CH_3) = (2.90 \pm 0.79) \times 10^{-11}$ and $k_2(OH + CH_2 = CHOC(O)CH_2CH_3) = (2.46 \pm 0.28) \times 10^{-11}$. This is the first kinetic study of title reactions under atmospheric conditions. The kinetic data were compared with previous literature values, used to calculate atmospheric lifetimes and correlated with the ionization potential of the unsaturated compounds.

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CHEMICAI PHYSICS L<u>ETTE</u>RS

1. Introduction

Unsaturated ketones and esters are carbonyl volatile organic compounds (VOC) released to the atmosphere by a variety of anthropogenic and biogenic sources such as the polymer industry and vegetation, respectively. On the other hand, they can be produced by the atmospheric degradation of isoprene, terpenes and other alkenes emitted from plants [1,2] and by the photodegradation of conjugated dienes from automobiles [3].

Ethyl vinyl ketone (EVK) (1-penten-3-one), which forms part of biogenic emissions, has shown to be released to the troposphere by stressed-induced emissions from different plants [4].

Vinyl ester compounds, with structure of CH₂==CHOC(O)R, are released mainly from industrial uses of polymers and resins. The sources of the emission of acetates and propionates, like vinyl propionate (VP), consist of manufacturers of plastics, aircraft and electronic components with wide applications as solvents and feedstocks [5].

The atmospheric sink of these unsaturated oxygenated compounds is photolysis and gas-phase reactions initiated by oxidants like OH radicals during day, NO₃ radicals at night and O₃ molecules. Furthermore, the formation of low-vapour pressure organic compounds, like carboxylic acids, may contribute to the formation of nucleus of condensation leading particle production [6].

In this sense, kinetic and mechanistic studies, under atmospheric conditions, are necessary to understand the effects of the VOCs degradation processes on the air quality.

The database on kinetic and product distribution studies of the reactions of unsaturated ketones and esters towards OH radicals is

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scarse, including a few calculated values from SAR relationships [7–13].

In this Letter we report the rate coefficients for the reactions of OH radicals with EVK (k_1) and VP (k_2) :

$OH + CH_2 = CHC(O)CH_2CH_3 \rightarrow Products$	(1)
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$OH + CH_2 = CHOC(0)CH_2CH_3 \rightarrow Products$ (2)

Experiments were performed using a collapsible Teflon chamber at room temperature and atmospheric pressure by the relative method with different reference compounds.

There is only a previous value of the rate constant of EVK with OH using a PLP system coupled with LIF detection of OH. To the best of our knowledge the rate coefficient for the reaction of OH radicals with VP has not been reported in the literature. Therefore, this is the first determination of the rate coefficient for the reaction of OH radicals with EVK at atmospheric pressure as well as the first kinetic determination of the reaction of OH radicals with VP.

The aim of the work is to gain a better understanding of the reactivity of the α , β -unsaturated oxygenated VOCs towards different tropospheric oxidants. This study also represents an extension of a previous work on the reactivity of OH towards unsaturated esters [7–10], Cl towards unsaturated carbonyls [14] and OH and Cl towards acrylic acid and acrylonitrile [15]. In conjunction with other available kinetic data, the rate coefficients obtained in this work, and other values from the literature for similar unsaturated esters and ketones, were correlated with the ionization potential (IP) of the α , β -unsaturated could be used to estimate rate coefficients for the reactions of similar compounds with OH radicals for which the rate coefficients have not been yet determined.

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In addition, the tropospheric implications of the reactions studied were assessed taking into account the residence lifetimes determined by the reactions with main tropospheric oxidants.

2. Experimental

The experimental set-up consisted of an 80 L Teflon bag located in a wooden box with the internal walls covered with aluminum foil, and operated at atmospheric pressure (750 ± 10) Torr and (298 ± 1) K.

The amounts of the organic reactants measured were flushed into the bag with a stream of air. The bag was then filled to its full capacity at atmospheric pressure with synthetic air. H₂O₂ was used to generate OH radicals by its photolysis using a set of germicidal lamps:

 $H_2O_2 \rightarrow 2OH$ (3)

These lamps provide UV-radiation with a λ maximum around 254 nm. In the present work, typically four of these lamps were used to produce OH radicals and the time of photolysis varied from 2 to 15 min.

Reaction mixtures consisting of a reference organic compound and the sample organic reactant, diluted in air, were prepared in the reaction chamber and left to mix, prior to photolysis, for approximately 1 h. Before each set of experiments, the bag was cleaned by filling it with a mixture of O_2 and N_2 photolyzed for 15–25 min using four germicidal lamps (Philips 30 W) with a UV emission at 254 nm, to produce O_3 . After this procedure, the bag was cleaned up again by repeated flushing with air and the absence of impurities was checked by gas chromatography before performing the experiments.

Gas samples were periodically removed from the Teflon bag using Hamilton gas-tight calibrated syringes. The organics were monitored by gas chromatography (Shimadzu GC-14B) coupled with flame ionization detection (FID), using a Porapak Q column (Alltech, 2.3 m) held from 140 to 180 °C.

In the presence of the oxidant OH radical the VOCs studied and the references decay through the following reactions:

$$OH + VOC \rightarrow Products$$
 (4)

$$OH + Reference \rightarrow Products$$
 (5)

Provided that the reference compound and the reactant are lost only by reactions (4) and (5), then it can be shown that:

$$\ln\left\{\frac{[\text{VOC}]_{0}}{[\text{VOC}]_{t}}\right\} = \frac{k_{4}}{k_{5}} \ln\left\{\frac{[\text{Reference}]_{0}}{[\text{Reference}]_{t}}\right\}$$
(6)

where, $[VOC]_0$, $[Reference]_0$, $[VOC]_t$ and $[Reference]_t$ are the concentrations of the VOC and the reference compound at times t = 0 and t, respectively, and k_4 and k_5 are the rate constants of reactions (4) and (5), respectively.

The relative rate technique relies on the assumption that the VOC and the reference compounds are removed solely by reaction with OH radicals. To verify this assumption, mixtures of hydrogen peroxide and air with the VOC of interest and the reference compound were prepared and allowed to stand in the dark for 2 h. In all cases, the reaction of the organic species with the precursor of OH (hydrogen peroxide), in the absence of UV light, was of negligible importance over the typical time periods used in this work.

Furthermore, to test for possible photolysis of the reactants used, mixtures of the VOCs in air, in the absence of hydrogen peroxide, were irradiated for 30 min using the output of all the germicidal lamps surrounding the chamber. No significant photolysis of any of the reactants was observed.

The initial concentrations used in the experiments were in the range of $59-124 \text{ ppm} = 2.46 \times 10^{13} \text{ molecule cm}^{-3}$ at

298 K and 760 Torr of total pressure) for the unsaturated VOCs, 74–198 ppm for diethyl ether, 3-chloropropene and 1,1-dichloroethene.

3. Materials

The following chemicals with purities as stated by the supplier were used without further purification: nitrogen (AGA, 99.999%), synthetic air (Air Liquide, 99.999%), ethyl vinyl ketone (Aldrich, 97%), vinyl propionate (Aldrich, 98%), diethyl ether (Fluka, 99%), 3-chloropropene (Fluka, 98%), 1,1-dichloroethene (Aldrich, 99.99%) and H_2O_2 (Cicarelli, 60% wt).

4. Results and discussion

Relative rate coefficients for the reactions of OH radicals with ethyl vinyl ketone and vinyl propionate were determined by comparing the OH reaction with the VOCs studied to that with the reference compounds from Eq. (6). The data were fitted to a straight line by the linear least-squares procedure.

The losses of EVK and VP by OH radicals are shown with different reference compounds in Figures 1 and 2. Figures 1 and 2 show only one example with two references for each reaction studied.

The following compounds were used as reference reactions to determine the rate coefficients of reactions (1) and (2):

$OH + CH_3CH_2OCH_2CH_3 \rightarrow Products$ ((7))
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OH	$+CH_2 = CH_2$	$CH_2Cl \rightarrow Products$	(8
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$$OH + CCl_2 = CH_2 \rightarrow Products$$
 (9)

where $k_7 = (1.36 \pm 0.11) \times 10^{-11}$ [16], $k_8 = (1.69 \pm 0.07) \times 10^{-11}$ [17] and $k_9 = (1.05 \pm 0.10) \times 10^{-11}$ [18]. All the *k* values are in units of cm³ molecule⁻¹ s⁻¹.

Table 1 shows the data on relative rate coefficients k_{VOC}/k_{ref} and absolute rate coefficients k_{VOC} at room temperature (298 K). The ratios were obtained from the average of several experiments using different initial concentrations of the reactants. The rate constants obtained by averaging the values from different experiments were the following:

$$k_1 = (2.90 \pm 0.79) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

 $k_2 = (2.46 \pm 0.28) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$



Figure 1. Plots of the kinetic data for the reaction of ethyl vinyl ketone with OH radicals using diethyl ether (\Box) and 1,1-dichloroethene (\bigcirc) as reference hydrocarbons.

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Figure 2. Plots of the kinetic data for the reaction of vinyl propionate with OH radicals using diethyl ether (\Box) and 3-chloropropene (\bigcirc) as reference hydrocarbons.

The errors quoted are twice the standard deviation arising from the least-squares fit of the straight lines, to which we have also considered the corresponding error on the reference rate constants (7)-(9).

In this work the reaction of OH radicals with EVK (1) was studied for the first time under atmospheric pressure using two different reference compounds, diethyl ether and 1,1-dichloroethene, with air as bath gas. In Table 2 are listed the value obtained for k_1 from this work in comparison with previous values from literature. The average of all the measurements yields $k_1 = (2.90 \pm 0.79) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ in agreement, within the experimental error, with the absolute value by the PLP–LIF technique of

Table 1

Rate constant ratio $k_{VOC}/k_{reference}$ and rate constants for the reaction of OH radicals with ethyl vinyl ketone and vinyl propionate at 298 ± 3 K in 760 ± 10 Torr of air.

VOC	Reference	$k_{\rm VOC/kref}$	$k_{VOC} (\times 10^{11})$ (cm ³ molecule ⁻¹ s ⁻¹)
CH ₂ =CHC(0)CH ₂ CH ₃	$\begin{array}{l} CH_2 = CCl_2\\ CH_2 = CCl_2\\ CH_3 CH_2 OCH_2 CH_3\\ CH_3 CH_2 OCH_2 CH_3\\ Average \end{array}$	$\begin{array}{c} (2.53 \pm 0.10) \\ (2.98 \pm 0.20) \\ (2.00 \pm 0.15) \\ (2.48 \pm 0.13) \end{array}$	$\begin{array}{l} (2.53 \pm 0.60) \\ (2.98 \pm 0.79) \\ (2.72 \pm 0.42) \\ (3.37 \pm 0.45) \\ (2.90 \pm 0.79) \end{array}$
CH ₂ =CHOC(0)CH ₂ CH ₃	CH ₂ =CHCH ₂ Cl CH ₂ =CHCH ₂ Cl CH ₃ CH ₂ OCH ₂ CH ₃ CH ₃ CH ₂ OCH ₂ CH ₃ Average	(1.35 ± 0.02) (1.47 ± 0.04) (1.92 ± 0.05) (1.80 ± 0.04)	$\begin{array}{l} (2.28 \pm 0.24) \\ (2.48 \pm 0.26) \\ (2.61 \pm 0.28) \\ (2.45 \pm 0.25) \\ (2.46 \pm 0.28) \end{array}$

Table 2

Comparison of the room temperature rate coefficients for the reaction of OH radicals with ethyl vinyl ketone informed in this work with previous reported determinations.

$k_{OH} imes 10^{11}$ (cm ³ molecule ⁻¹ s ⁻¹)	Technique	Reference
(2.90 ± 0.79)	RM–GC	This work
(2.36 ± 0.47)	PLP–LIF	[12]
2.49	SAR estimation	[19]
3.6	SAR estimation	[20]

RM-GC, Relative method-gas chromatography; PLP-LIF, Pulsed laser photolysislaser induced fluorescence; SAR, Structure activity relationship. $(2.36 \pm 0.47) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ previously reported. Furthermore, our value agrees with the two different previous SAR estimations, [19,20] being in between of both of these reported values of 2.49 and 3.6 (in units of 10^{11} cm³ molecule⁻¹ s⁻¹).

To the best of our knowledge, no values of the rate constants for the reaction (2) of OH radicals with vinyl propionate have already been reported. Thus, this study is the first kinetic study of these reactions and therefore, no direct comparison with the literature can be made.

The reactivity of the OH radicals with ethene and methyl substituted alkenes has been found to correlate with the ionization potential (IP) of the olefins. The energy required to remove a π electron, the ionization potential [21] is lowered in the olefins by substitution of an H atom by an alkyl group, while the electron density of the double bond is increased by the substitution, leading to an increase in the reaction rates. Thus, the use of the rate coefficients determined in this work, together with values of different unsaturated carbonyl compounds and acrylonitrile from the literature, enables a relationship with the IP for the reactions of OH radicals with unsaturated carbonylic VOCs. This correlation is shown in Figure 3. The ionization potentials (IP) for the unsaturated VOCs were calculated using the GAUSSIAN 03 package. The geometry optimizations and initial values of energies were obtained at the Hartree-Fock (HF) level, and ab initio Hamiltonian with a 6-31++ G(d,p) basis sets. The self-consistent field energies were then calculated by Moller-Plesset perturbation theory (MP4-SCF) using an ab initio Hamiltonian with a 6-311++G(d,p) basis sets. The correlation obtained for this group of reactions is as follows:

$$k \times 10^{11} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} = -1.06 \times \text{IP (eV)} + 12.81$$
 (10)

The good quality of this correlation is such that estimations can be made of the rate coefficients for reactions of OH with unsaturated carbonyl VOCs, not yet investigated.

Atmospheric lifetimes, τ_x , of the VOCs studied in this work were calculated through the expression: $\tau_x = 1/k_x[X]$ with X = OH, NO₃ and Cl. Table 3 lists the atmospheric lifetimes with respect to the reaction with OH radicals, NO₃ radicals and Cl atoms for the unsaturated VOCs. For the calculations the following rate coefficients values were used: $k_1 = 2.90 \times 10^{-11}$ and $k_2 = 2.46 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ from this work, $k(NO_3 + EVK) = 9.4 \times 10^{-17}$ [13], $k(Cl + EVK) = 2.91 \times 10^{-10}$ [23] and $k(Cl + VP) = 2.06 \times 10^{-10}$ [23].



Figure 3. Plot of the room temperature rate coefficients for the reactions of OH radicals with unsaturated esters and ketones from this work and literature. The IP were calculated using the GAUSSIAN 03 package and the rate coefficients were obtained from Ref. [22].

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Table 3

VOC

CH2=CHC(0)CH2CH3

gen peroxide.

CH2=CHOC(0)CH2CH3

Estimated tropospheric lifetimes of the unsaturated carbonyl compounds studied in this work with OH radicals, NO_3 radicals and Cl atoms.

 τ_{NO3}

16

(hours)

6

 τ_{OH}

5

6

(hours)

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Typical oxidant concentrations were used: a 12 h average OH radical concentration of $[OH] = 2 \times 10^6$ radicals cm⁻³ (day-time) [24]; $[NO_3] = 5 \times 10^8$ radicals cm⁻³ (night-time) [25] and [CI] = 1 × 10⁴ atoms cm⁻³ [26]. Other process like photolytic loss of the esters and VP will be negligible, since as we pointed out previously, they are photolytically stable in the actinic region of the electromagnetic spectrum [7,8,12]. Furthermore, this statement was also confirmed by the negligible depletion of the chromatographic areas corresponding to the unsaturated photolysis of the VOCs in the absence of hydro-

Unfortunately, no data are available on the reactions of NO₃ radicals with VP or EVK and VP with O₃ molecules. However, on the basis of structural similarities it is probable that will show a reactivity towards NO₃ radicals similar to that of EVK. Therefore the lifetimes indicate that the esters are likely to be removed rapidly in the gas phase, the reaction with OH being the major loss process for both compounds studied during day and with NO₃ radicals at night. The short lifetimes for EVK and VP, in the range of few hours, implies that they are likely to be removed rapidly in the gas phase close to their source of emission.

Further work concerning product studies at different NOx, concentrations, pressure and temperature conditions is required to postulate the atmospheric degradation pathways of terminal carbonyl unsaturated compounds in the troposphere. Kinetic information, together with product information of the reactions of these carbonyl compounds with OH radicals, is necessary to evaluate their impact on air quality, their influence on the atmospheric oxidation capacity and on their possible contribution to the SOA formation.

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