



Research paper

Kinetics of OH- and Cl-initiated oxidation of $\text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3$ and $\text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3$ and fate of the alkoxy radicals formed

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ABSTRACT

Rate coefficients of the reactions of OH and Cl radicals with vinyl and allyl butyrate were determined for the first time at 298 K and 1 atm using the relative method to be (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_1(\text{OH} + \text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3) = (2.61 \pm 0.31) \times 10^{-11}$, $k_2(\text{Cl} + \text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3) = (2.48 \pm 0.89) \times 10^{-10}$, $k_3(\text{OH} + \text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3) = (2.89 \pm 0.31) \times 10^{-11}$, and $k_4(\text{Cl} + \text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3) = (2.25 \pm 0.96) \times 10^{-10}$. Reactivity trends and atmospheric lifetimes of esters are presented. Additionally, a product study shown butyric acid and polyfunctional products for the reactions of vinyl and allyl butyrate, respectively and general mechanism is proposed.

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1. Introduction

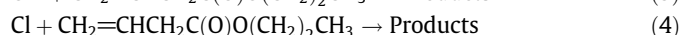
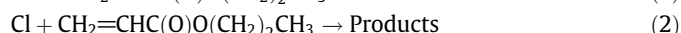
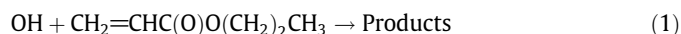
It is widely known that esters are emitted to the atmosphere in large quantities, either from natural or anthropogenic sources and are also formed by the oxidation of ethers. Esters are present in pheromones, fruits and essential oils, and they have pleasant odors. For these reasons are often added to consumer products to provide a pleasant odor [1]. Unsaturated esters are also emitted from the industry, as vinyl butyrate (VB) that is used for synthetic production base materials in foods or beverages [2]. Moreover allyl butyrate (AB) is widely used in the synthesis of polymers and copolymers as well as in the food industry as a flavoring [3,4].

Widespread use of the esters by industry inevitably results in fugitive emissions of the compounds to the atmosphere. Once in the atmosphere, these unsaturated esters, will be subjected to degradation through reaction with tropospheric oxidants, *i.e.*, mainly with OH radicals, NO_3 radicals, Cl atoms and O_3 . Since the unsaturated esters will be mainly emitted in industrial centers and urban areas, their expected relatively fast reactions with tropospheric oxidants due to the presence of the double bond.

Kinetic data and mechanistic information on the important atmospheric degradation pathways of unsaturated esters are essential components in any attempts to reliably assess the possible contribution of these substances to the severe photochemical air pollution which is frequently experienced in urban and regional areas.

In this study it has been reported the rate coefficient of the reaction of vinyl butyrate ($\text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3$) and allyl butyrate

($\text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3$) with OH radicals and Cl atoms at 298 K and 760 Torr:



There are only previous values of the rate coefficients of the reactions of similar acetates and propionate (vinyl acetate, vinyl propionate and allyl acetate) with OH radicals and Cl atoms using the relative kinetic methods [5–9]. Although, there are several kinetic studies of the OH-radical [10–12], O_3 -molecule [13–16], Cl-atom [17,18] and the NO_3 -radicals [19–21] initiated oxidation of other unsaturated esters.

To the best of our knowledge the rate coefficients for the reactions of OH radicals and Cl atoms with butyrates, including VB and AB, have not been previously reported in the literature. Hence, this is the first determination of the rate coefficient for the reaction of OH radicals and Cl atoms with VB and AB at atmospheric pressure.

These studies were performed using a collapsible Teflon chamber at atmospheric conditions by the relative method using difference reference compounds. Kinetics results are rationalized in terms of reactivity trends by comparison with others unsaturated esters.

In addition, product studies using the GC–MS technique under atmospheric conditions were carried out for the title reactions and the degradation pathways in the atmosphere are also discussed. Atmospheric lifetimes of the Volatile Organic Compounds (VOCs) studied in this work were calculated taking into account the experimental rate coefficients obtained in this work.

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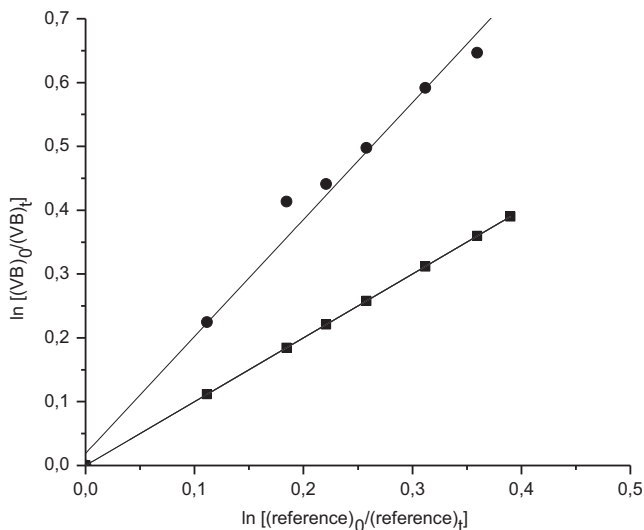


Fig. 1. Relative kinetic plot of the reaction of OH radical with Vinyl Butyrate using 3-Chloropropene (●) and Methyl Methacrylate (■) as references at 298 K and 760 Torr.

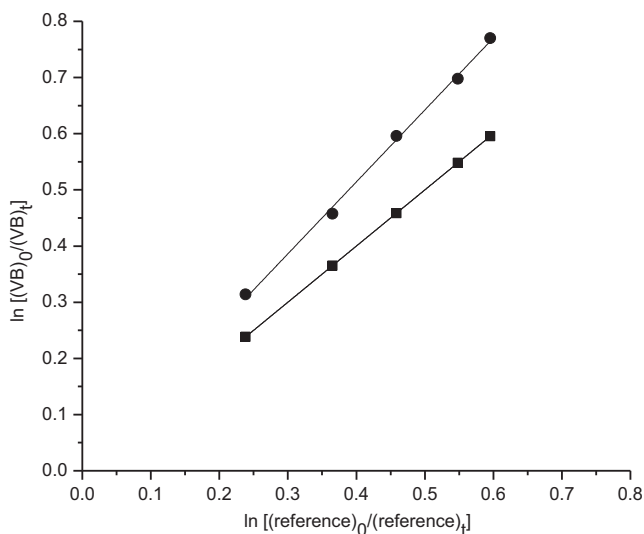
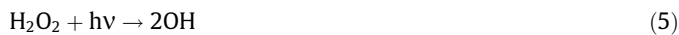


Fig. 2. Relative kinetic plot of the reaction of Cl atoms with Vinyl Butyrate using (●) Vinyl Propionate and Methyl Methacrylate (■) as references at 298 K and 760 Torr.

2. Experimental

The experiments were performed in a Teflon bag of 80-l placed in a wooden box with the internal walls covered with aluminum foil. Organic reactants were measured from calibrated bulbs and were introduced into the bag through a stream of nitrogen. Then, the bag was filled to its full capacity at atmospheric pressure with nitrogen.

OH radicals were generated by UV irradiation at 254 nm of H_2O_2 :



Cl atoms were generated by photolysis at 254 nm of $ClC(O)C(O)Cl$:

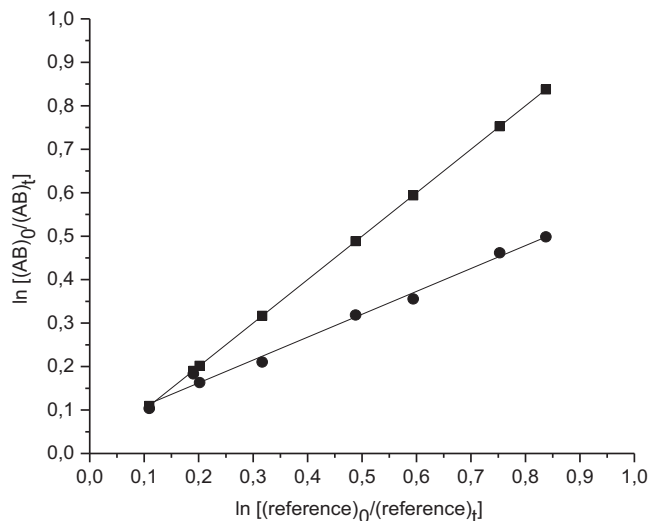


Fig. 3. Relative kinetic plot of the reaction of OH atoms with Allyl Butyrate using (●) 2-Methyl-3-buten-2-ol and Methyl Methacrylate (■) as references at 298 K and 760 Torr.

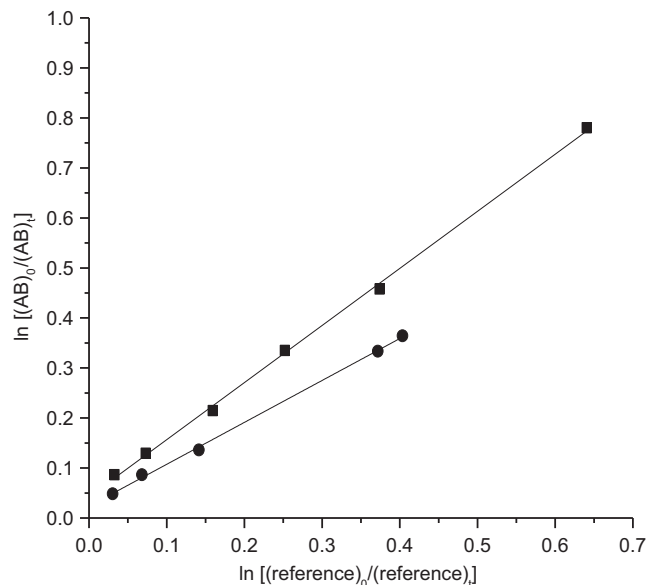


Fig. 4. Relative kinetic plot of the reaction of Cl atoms with Allyl Butyrate using (■) Vinyl Propionate and Methyl Methacrylate (●) as references at 298 K and 760 Torr.

Before each experiment, the bag was cleaned by filling it with a mixture of O_2 and N_2 which was photolyzed for 15 min using 6 germicidal lamps (Philips 30 W) with a UV emission at 254 nm, to produce O_3 . After this procedure, the bag was cleaned again by repeated flushing with N_2 and checked before performing the experiments by gas chromatography that there were no observable impurities.

Gas samples were taken from the Teflon bag using calibrated gas syringes. The organic compounds were monitored by gas chromatography (Shimadzu GC-14B) coupled with flame ionization detection (FID), using a Porapak Q column (Alltech, 2.3 m) held at a temperature of 200 °C for these compounds.

In the presence Cl atom or OH radical, vinyl butyrate (VB), allyl butyrate (AB) and the references decay through the following reactions:

Table 1
Reference compound, measured rate coefficient ratios, $k_{\text{voc}}/k_{\text{reference}}$, and the obtained rate coefficients for the reactions of OH radicals and Cl atoms with VB and AB at 298 K.

Unsaturated ester	Reference	$k_{\text{voc}}/k_{\text{reference}}$	k ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}=\text{CH}_2 + \text{OH}$	3-Chloropropene	(1.60 ± 0.07)	$(2.70 \pm 0.23) \times 10^{-11}$
	3-Chloropropene	(1.61 ± 0.04)	$(2.72 \pm 0.18) \times 10^{-11}$
	Methyl Methacrylate	(0.58 ± 0.03)	$(2.40 \pm 0.31) \times 10^{-11}$
	Methyl Methacrylate	(0.63 ± 0.02)	$(2.61 \pm 0.28) \times 10^{-11}$
	Average		$(2.61 \pm 0.31) \times 10^{-11}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}=\text{CH}_2 + \text{Cl}$	Methyl Methacrylate	(0.87 ± 0.03)	$(2.45 \pm 0.89) \times 10^{-10}$
	Methyl Methacrylate	(0.79 ± 0.01)	$(2.22 \pm 0.76) \times 10^{-10}$
	Vinyl Propionate	(1.28 ± 0.03)	$(2.59 \pm 0.52) \times 10^{-10}$
	Vinyl Propionate	(1.30 ± 0.02)	$(2.67 \pm 0.51) \times 10^{-10}$
	Average		$(2.48 \pm 0.89) \times 10^{-10}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2 + \text{OH}$	2-Methyl-3-buten-2-ol	(0.52 ± 0.01)	$(2.94 \pm 0.12) \times 10^{-11}$
	2-Methyl-3-buten-2-ol	(0.50 ± 0.01)	$(2.83 \pm 0.12) \times 10^{-11}$
	Methyl Methacrylate	(0.70 ± 0.02)	$(2.90 \pm 0.31) \times 10^{-11}$
	Methyl Methacrylate	(0.70 ± 0.02)	$(2.90 \pm 0.31) \times 10^{-11}$
	Average		$(2.89 \pm 0.31) \times 10^{-11}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2 + \text{Cl}$	Methyl Methacrylate	(0.83 ± 0.01)	$(2.34 \pm 0.79) \times 10^{-10}$
	Methyl Methacrylate	(0.83 ± 0.07)	$(2.34 \pm 0.96) \times 10^{-10}$
	Vinyl Propionate	(0.99 ± 0.05)	$(2.34 \pm 0.45) \times 10^{-10}$
	Vinyl Propionate	(1.10 ± 0.01)	$(2.27 \pm 0.41) \times 10^{-10}$
	Average		$(2.25 \pm 0.96) \times 10^{-10}$

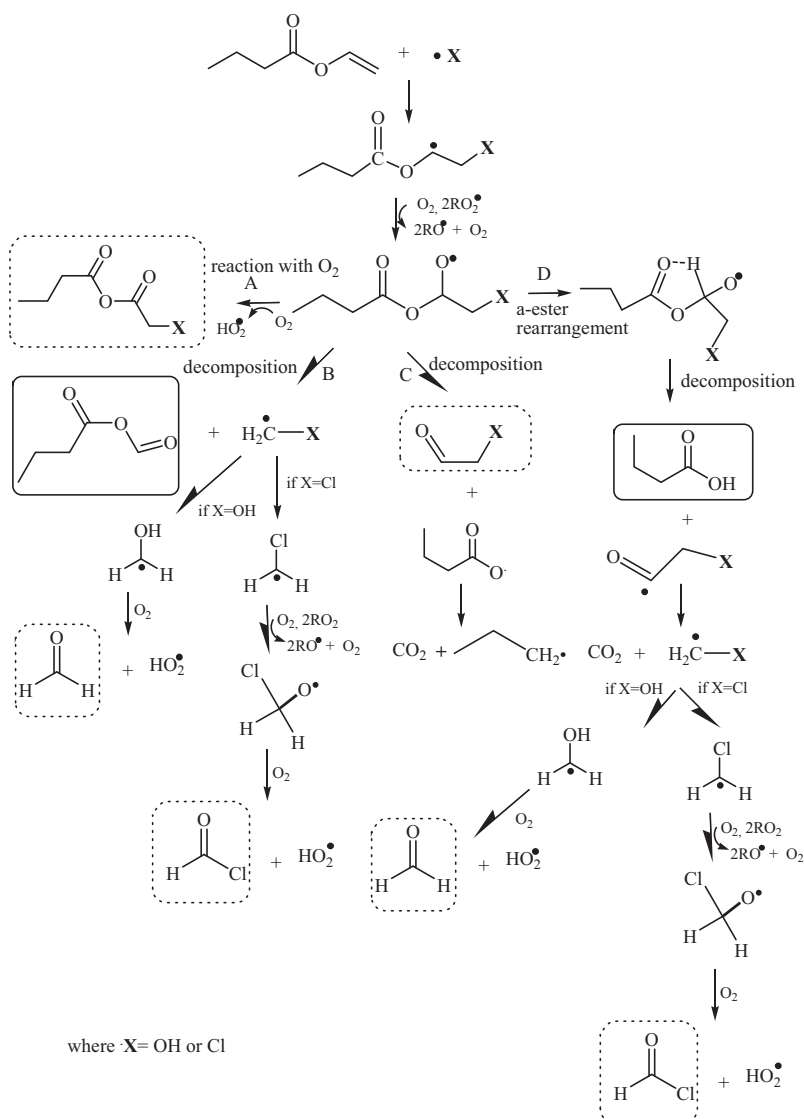


Fig. 5. Simplified mechanism for the OH radical/Cl atom initiated oxidation of Vinyl butyrate ($\text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3$) via addition of OH/Cl to the terminal carbon of the double bond. The identified products are showed in filled line.

Table 2

Comparison of the experimental (k_{exp}) for the reaction of OH with unsaturated esters and calculated by US EPA AOPWIN (k_{calc}) at atmospheric conditions rate coefficients.

Unsaturated ester	k_{calc} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)	k_{exp} ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) ^a
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}=\text{CH}_2$	2.79×10^{-11}	$(2.61 \pm 0.31) \times 10^{-11}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$	2.94×10^{-11}	$(2.89 \pm 0.31) \times 10^{-11}$

^a This work.

Table 3

Estimated tropospheric lifetimes of the butyrates studied in this work with different troposphere oxidants.

VOC	τ_{OH}^a (h)	τ_{Cl}^a (days)
Vinyl butyrate	5	5
Allyl butyrate	5	5

$\tau_{\text{OH}}=1/k(\text{voc})[\text{OH}]$, $\tau_{\text{Cl}}=1/k(\text{voc})[\text{Cl}]$. Typical atmospheric concentrations were used, $[\text{OH}] = 2 \times 10^6 \text{ molecule cm}^{-3}$ [36] and $[\text{Cl}] = 1 \times 10^4 \text{ molecule cm}^{-3}$ [37].

^a This work.



Provided that the reference compound and the reactant are lost only by reactions (7) and (8), then it can be shown that:

$$\ln \left\{ \frac{[\text{VOC}]_0}{[\text{VOC}]_t} \right\} = \frac{k_7}{k_8} \ln \left\{ \frac{[\text{Reference}]_0}{[\text{Reference}]_t} \right\} \quad (9)$$

where $[\text{VOC}]_0$, $[\text{Reference}]_0$, $[\text{VOC}]_t$ and $[\text{Reference}]_t$ are the concentrations of the vinyl butyrate, allyl butyrate and references compounds at times $t = 0$ and t , respectively, and k_7 and k_8 are the rate coefficients of reactions (7) and (8), respectively.

The relative rate technique relies on the assumption that both VOCs and the reference organics are removed solely by reaction with the oxidant species (Cl or OH). To verify this assumption, mixtures of oxalyl chloride or hydrogen peroxide with N_2 and both organics were prepared and allowed to stand in the dark for two hours. In all cases, the reaction of the organic species with the precursor of Cl or OH ($\text{ClC}(\text{O})\text{C}(\text{O})\text{Cl}$ or H_2O_2), in the absence of UV light, was of negligible importance over the typical time periods used in this work.

In addition, to test for possible photolysis of the reactants used, mixtures of VB or AB in nitrogen, in the absence of oxidants, were irradiated using the output of all germicidal lamps surrounding the chamber for 30 min. It was not observed the photolysis of reactants.

The initial concentration used in the experiments were in the range of 200–220 ppm (1 ppm = $2.46 \times 10^{13} \text{ molecule cm}^{-3}$ at 298 K and 760 Torr of total pressure) for VB and AB. The concentration of H_2O_2 ranged from 50 to 120 ppm and $\text{ClC}(\text{O})\text{C}(\text{O})\text{Cl}$ 160–180 ppm in around 760 Torr of N_2 .

For identification of the products formed, after irradiation, the GC–MS analytical technique was employed using a Shimadzu GC–MS QP 5050 spectrometer equipped with a capillary column VF-5MS (5% phenyl, 95% dimethylpolysiloxane) of 30 m–0.25 mm. Gas samples were removed from the Teflon chamber using solid phase microextraction (SPME) as a preconcentration technique of the analytes. The SPME technique involves the extraction of analytes from the sample matrix using a fused silica fiber generally cover whit an absorbent polymer, followed by desorption of analytes by the temperature on the injection port.

In this study we have used the [divinylbenzene/Carboxen/poly dimethylsiloxane] (DVB/CAR/PDMS) fiber for these compounds. The exposure time was 10 min, and 2 min of desorption in the injection port.

3. Materials

It have been used the following chemicals with purities declared by the supplier: N_2 (AGA, 99.999%), synthetic air (Air Liquide, 99.999%), vinyl butyrate (Aldrich, 99%), allyl butyrate (Aldrich, 98%), 3-chloropropene (Fluka, 98%), methyl methacrylate (Aldrich, 99%), vinyl propionate (Aldrich, 98%), 2-methyl-3-buten-2-ol (Aldrich, 96%), acrylonitrile (Baker, 99.5%), oxalyl chloride (Aldrich, 99%) and hydrogen peroxide (Ciccarelli, 60 wt%).

4. Results and discussion

Relative rate coefficients for the reactions of OH radicals and Cl atoms with VB and AB were determined. The data were fitted to a straight line by the linear least-squares procedure.

The losses of VB and AB by OH radicals and Cl atoms are shown with different reference compounds in Figs. 1–4. For each reaction studied four runs were performed for the rate coefficient determination; nevertheless, only one example is displayed in Figs. 1–4.

The data on relative rate coefficients ($k_{\text{VB}}/k_{\text{Reference}}$, $k_{\text{AB}}/k_{\text{Reference}}$) and the absolute rate coefficients k_{VB} and k_{AB} at room temperature (298 K) are presented in Table 1. The ratios were obtained from the average values using different initial concentrations of the reactants. It is gratifying to note the agreement between the experiments conducted with different reference compounds. The rate coefficients obtained by averaging the values from different experiments were the following:

$$k_{\text{OH}+\text{VB}} = (2.61 \pm 0.31) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

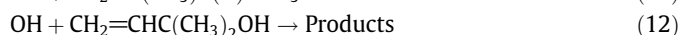
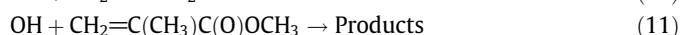
$$k_{\text{Cl}+\text{VB}} = (2.48 \pm 0.89) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{OH}+\text{AB}} = (2.89 \pm 0.31) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{Cl}+\text{AB}} = (2.25 \pm 0.96) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

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

The following compounds were used as reference reactions: 3-chloropropene, methyl methacrylate, 2-methyl-3-buten-2-ol, vinyl propionate and acrylonitrile to determine the rate coefficient of the reactions (1) and (4):



where $k_{10} = (1.69 \pm 0.07) \times 10^{-11}$ [22], $k_{11} = (4.15 \pm 0.32) \times 10^{-11}$ [11], $k_{12} = (5.67 \pm 0.13) \times 10^{-11}$ [23], $k_{13} = (2.82 \pm 0.93) \times 10^{-10}$ [17], $k_{14} = (2.06 \pm 0.36) \times 10^{-10}$ [9], $k_{15} = (1.11 \pm 0.23) \times 10^{-10}$ [24]. All the k values are in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

To the best of our knowledge, there are no other prior reported values of the rate coefficients for the reactions (1)–(4) of OH radicals and Cl atoms with vinyl and allyl butyrate. Thus, the present work is the first kinetic study of these reactions and therefore no direct comparison with the literature could be made.

For the reactions with OH radicals, the reactivity of the unsaturated esters are higher than the analogues saturated, where $k_{\text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3} = 2.61 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this work) $>$ $k_{\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3} = 0.44 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [25] and $k_{\text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3} = 2.89 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this work) $>$ $k_{\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3} = 0.742 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [26]. Also it is possible to observe that rate coefficients with OH radicals are similar to those of the corresponding alkenes:

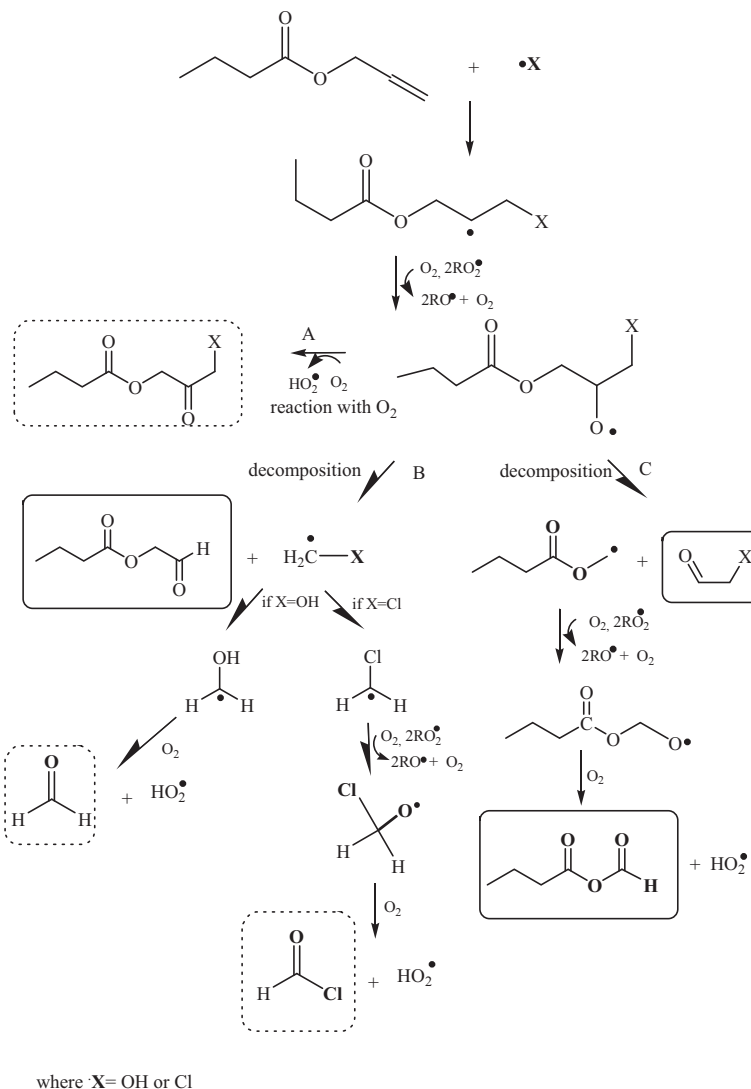


Fig. 6. Simplified mechanism for the OH radical/Cl atom initiated oxidation of Allyl butyrate ($\text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3$) via addition of OH/Cl to the terminal carbon of the double bond. The identified products are showed in filled line.

$k_{\text{CH}_2=\text{CHC}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3} = 2.61 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this work) \sim $k_{\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{CH}_3} = 2.74 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [27] and $k_{\text{CH}_2=\text{CHCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_2\text{CH}_3} = 2.89 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this work) \sim $k_{\text{CH}_2=\text{CHCH}_2(\text{CH}_2)_2\text{CH}_3} = 3.69 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [28]. This indicates that the reactions of OH with unsaturated esters proceed mainly by OH addition to the >C=C< bonds, forming a 1,2-hydroxyalkyl radical which then reacts with O_2 to form the corresponding 1,2-hydroxyalkylperoxy radical. At room temperature, H-atom abstraction, is minor, being $<5\text{--}10\%$ from the methyl-substituted [29].

On the other hand, in the Cl-initiated degradation reaction, the effect of the substituents on the reactivity is not significant as for the reactions initiated by OH radicals, possibly due to the addition of Cl atoms are less selective and their reactions are close to the collision gas theory limit as observed in addition reactions to other unsaturated VOCs [8,9].

Structure activity relationships (SAR), using the 'Environmental Protection Agency' rate constant calculation software, AOPWIN v1.91 [30] based on the SAR method developed by Kwok and Atkinson [31], were used to calculate the rate coefficients for the reactions of OH with the unsaturated ester studied. The results are shown in Table 2 and it is possible to observe that the values

obtained by calculations SAR are very close and within experimental error with the values reported in this work.

4.1. Product identification

As already mentioned OH radical and Cl atoms reactions with vinyl and allyl butyrate proceed mainly by initial addition of OH/Cl to the >C=C< bonds. In the absence of NO_x , the peroxy radicals will undergo self- and cross-peroxy reactions which will result, in the formation of 1,2-alkoxy radicals, nevertheless, molecular channel are also possible which will result in the formation of multifunctional products containing hydroxy/chlorine, carbonyl and ester functionalities [32,33].

It is known that, under atmospheric conditions, the alkoxy radical could react with O_2 forming HO_2 radical and the corresponding carbonyl compound; undergo β -scission forming a carbonyl compound and another radical; and undergo hydrogen shift isomerization forming dihydroxy/chlorine substituted radical [34,35]. Furthermore, the alkoxy radical with the structure $\text{RC}(\text{O})\text{OCH}(\text{O}')\text{R}'$ can undergo a fast rearrangement involving hydrogen transfer to the carbonyl group and further decomposition to

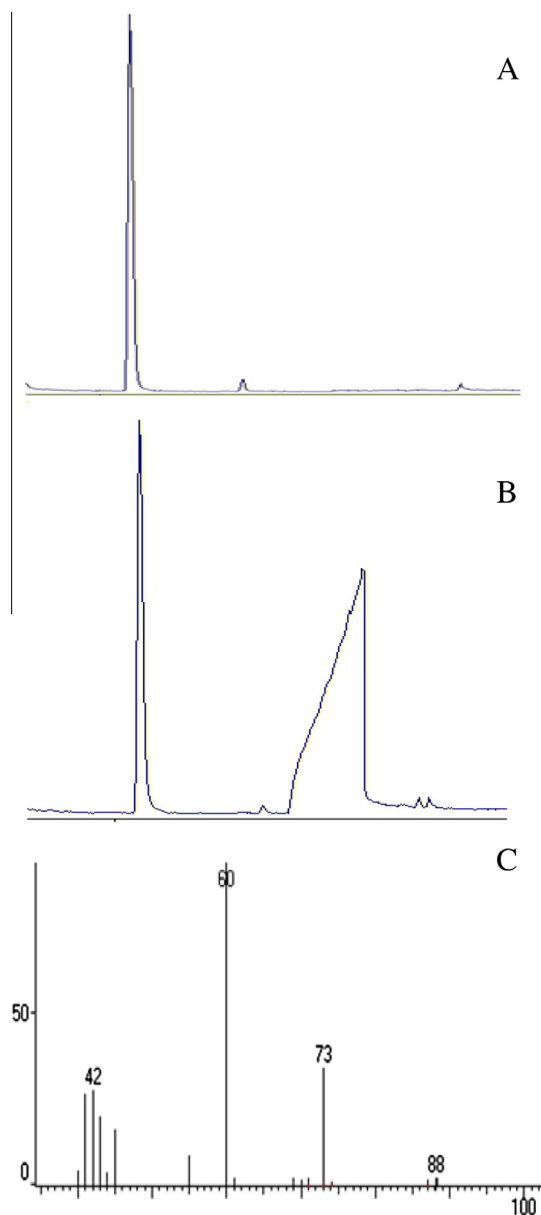


Fig. 7. Example of GC–MS chromatogram of a mixture of VB with H_2O_2 in air at 298 K and atmospheric pressure. A – Chromatogram obtained before photolysis where the reactant (VB) was observed (retention time 5.3 min). B – Chromatogram obtained after photolysis where butanoic acid was observed at 7.5 min. C – Mass spectrum for the butanoic acid with 7.5 min retention time.

produce the corresponding carboxylic acid $\text{RC}(\text{O})\text{OH}$ and a $\text{R}'\text{C}(\cdot)=\text{O}$ radical, through, an α -ester rearrangement reaction [35].

Simplified exemplary reaction mechanisms for the addition reactions of X radicals (where X = OH or Cl) with VB and AB in absence of NO_x are show in Figs. 5 and 6, respectively.

For VB + OH/Cl reaction, the alkoxy radical formed $(\text{CH}_3(\text{CH}_2)_2\text{C}(\text{O})\text{OC}(\text{O}\cdot)\text{HCH}_2\text{X})$, under atmospheric conditions could react through different pathways: (A) react with O_2 forming HO_2 radical and the corresponding hydroxy/halo anhydride; (B) undergo to decomposition forming an anhydride and hydroxy/halo alkyl radical; (C) for decomposition forming an hydroxy/chloro acetaldehyde and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}\cdot$ radical which leads to the formation of carbon dioxide and $\text{CH}_3\text{CH}_2\text{CH}_2$ radical. And (D) an α -ester rearrangement to lead butyric acid $(\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OH})$.

For AB + OH/Cl reaction, the alkoxy formed $(\text{CH}_3(\text{CH}_2)_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O}\cdot)\text{HCH}_2\text{X})$ could: (A) react with O_2 forming a hydroxy/

chloro dicarbonyl compound and HO_2 ; (B) undergo decomposition forming a dicarbonyl compound and another radical and (C) for decomposition forming to hydroxy/halo carbonyl compound and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2$ radical that further oxidation and reaction with O_2 leads to the formation of an anhydride.

In accordance with the products observed the fate of the alkoxy radicals formed in the OH + VB reaction seems to be the α -ester rearrangement, where the OH attacks mainly the terminal carbon of the double bond. CG–MS experiments shown butanoic acid as the main product (with fragments of m/z 42, 60, 73 and 88, characteristic of this kind of compounds). An example of the chromatogram obtained is showed in Fig. 7.

Identification of butanoic acid is in agreement with our previous product study for the reaction of vinyl acetate with OH radicals performed in a 1080 L quartz reactor using Fourier Transform Infrared Spectroscopy (FTIR) at 298 K and atmospheric pressure and in the absence of NO_x [32]. In this study, we have reported a product yield of $(28 \pm 5)\%$ for the formation of formic acetic anhydride, $(52 \pm 8)\%$ for formaldehyde and $(87 \pm 12)\%$ for acetic acid, indicating that the formation of a carboxylic acid, through an α -ester rearrangement of the hydroxyalkoxy radical formed, was the main fate this radical under these experimental conditions.

For the reaction of OH + AA, formyl methyl butyrate $(\text{CH}_3(\text{CH}_2)_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{H})$ was observed with ions of $m/z = 29, 31, 39, 43, 99$ and 101 in agreement with our previous work for the reaction of allyl acetate with OH radicals [32]. The formation of this polyfunctional compound could be explained by the decomposition of the alkoxy radical formed (Fig. 6, channel B).

Further experiments were also conducted to identify reaction products under similar conditions to the OH-products identification experiments for the reactions of VB + Cl and AA + Cl.

For the reactions of Cl atoms with VB, butanoic acid and formic butanoic anhydride $(\text{CH}_3(\text{CH}_2)_2\text{C}(\text{O})\text{OC}(\text{O})\text{H})$ were observed with ions with $m/z = 42, 60, 73, 88$ and 43, 57, 71, 85, 97, 128, respectively. The butanoic acid observed could be explained trough the α -ester rearrangement of the chloroalkoxy radical formed (Fig. 5, channel D). The formation of $(\text{CH}_3(\text{CH}_2)_2\text{C}(\text{O})\text{OC}(\text{O})\text{H})$ could be attributed to the decomposition of $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OC}(\text{O}\cdot)\text{CH}_2\text{Cl}$ radical (Fig. 5, channel B). These results are in agreement with our previous studies for the products distribution of the reaction of vinyl acetate with Cl atoms using a 1080 L quartz photoreactor coupled with FTIR spectroscopy as detection system [33].

Concerning of the products identification analysis for the reaction of AA + Cl, the presence of the dicarbonyl compound $(\text{CH}_3(\text{CH}_2)_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{H})$ could be explained by the decomposition of the chloroalkoxy radical formed (Fig. 6, channel B). In addition, we have observed the formation of formic butanoic anhydride and its co-product $(\text{CH}_2\text{ClC}(\text{O})\text{H})$, chloroacetaldehyde with ions with $m/z = 43, 57, 71, 85, 97, 128$ and 50, 60, 78, 93, 105, respectively. The formation of the anhydride and chloroacetaldehyde could be attributed the decomposition of the $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O}\cdot)\text{CH}_2\text{Cl}$ radical (Fig. 6, channel C).

The yields of the products formed from the OH and Cl photo-oxidation of the VB and AA studied here, however, still remains to be elucidated.

Further quantitative products distribution experiments for the reactions studied would be desirable to obtain a better understanding of the atmospheric implications associated with the widespread use of the unsaturated VOCs on air quality and their contribution to the formation of photochemical smog.

5. Atmospheric implications

Atmospheric lifetimes, τ_x , of the VB and AB studied in this work were calculated through the expression: $\tau_x = 1/k_x [\text{X}]$ with X = OH, Cl. Table 3 lists the atmospheric lifetimes with respect to the

reaction with OH radicals and Cl atoms for the butyrates studied in this work. Tropospheric lifetimes were calculated, considering a 12 h average concentration of OH of 2×10^6 molecule cm^{-3} [36]. Also it considered a global average chlorine concentration of 1×10^4 atoms cm^{-3} [37]. The lifetime of the reaction of VB with OH radicals and the corresponding lifetimes for the reaction with Cl atoms are 5 h and 5 days, respectively. For AB, we have obtained a lifetime of 5 h for reactions with OH and 5 days for reactions with Cl. Unfortunately no kinetic data is available for the reaction of these compounds with other oxidants as NO_3 radicals or O_3 molecules. There are only previous estimations for the lifetime of vinyl acetate regarding to the reaction of NO_3 radicals with a lifetime of 4 h [38] and lifetimes of 5 and 7 days for the reaction of O_3 molecules with vinyl and allyl acetate, respectively [39]. On the basis of structural similarities, it is probable that VB and AB will show a similar reactivity toward NO_3 radicals and O_3 molecules as vinyl and allyl acetate and thus have a similar lifetime with respect to reactions with these oxidants. Therefore, reactions with both OH and NO_3 radicals are also likely to be important removal processes for VB and AB.

The short lifetimes calculated for these compounds indicate that they may be degraded close to the emission source areas, causing a local impact potentially leading photo-oxidants in the atmosphere, responsible for the formation of photochemical smog. In agreement with previous studies, photolytic losses of the esters are negligible, and losses by uptake in surface on rainwater and cloud droplets are not important sinks for these kinds of compounds [7].

It is possible to observe that the main tropospheric degradation pathway for the compounds studied is the reaction with OH radical. Although, in marine and certain continental areas, Cl-atom initiated reactions could compete with the OH reaction.

In the reaction of VB with OH and Cl, we have identified butanoic acid and its precursors anhydrides, that do not absorb significantly at wavelengths greater than 250 nm, therefore, do not undergo photolysis in the troposphere, also are water-soluble, have low vapor pressures and are ubiquitous components of atmospheric aerosols. The solubility of carboxylic acid it is presented using Henry's law, butanoic acid Henry's law constant is 4.7×10^3 M atm^{-1} [40]. Species with Henry's law constant below approximately 10^3 M atm^{-1} will partition strongly into the atmospheric gas phase and wet/dry deposition will probably not be of mayor importance [40].

On the other hand, formaldehyde formed in atmospheric degradation of VOCs is one of the most reactive and important species in tropospheric photochemistry and ozone formation [1]. Carboxylic acids could be removed by reaction with OH as well as by wet or dry deposition. As a result, these acids are a common component of rain, clouds, fogs, and dews, and are found in the condensed phase from remote to highly polluted urban areas.

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