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## Tropospheric chemical degradation of vinyl and allyl acetate initiated by Cl atoms under high and low NO<sub>x</sub> conditions†

María B. Blanco,<sup>a</sup> Iustinian Bejan,<sup>bc</sup> Ian Barnes,<sup>\*b</sup> Peter Wiesen<sup>b</sup>  
and Mariano A. Teruel<sup>\*a</sup>

The products of the reactions of Cl atoms with vinyl acetate (VA) and allyl acetate (AA) have been investigated in a 1080 L chamber using *in situ* FTIR. The experiments were performed at 296 K and atmospheric pressure of synthetic air in the presence and in the absence of NO<sub>x</sub>. For the reaction of Cl with VA in the presence of NO<sub>x</sub> formic acetic anhydride, acetic acid and formyl chloride are the major reaction products. In the absence of NO<sub>x</sub>, the yields of these products are significantly reduced and formation of the carbon-chain-retaining compound CH<sub>3</sub>C(O)OC(O)CH<sub>2</sub>Cl is observed. For the reaction of Cl with AA in the presence of NO<sub>x</sub> acetoxyacetaldehyde and formaldehyde were observed as the main products. In contrast, without NO<sub>x</sub>, the observations support that the major reaction pathway is the formation of the carbon-chain-retaining compound CH<sub>3</sub>C(O)OCH<sub>2</sub>C(O)CH<sub>2</sub>Cl. The reaction mechanisms leading to the products are discussed. The formation of the high yields of formyl chloride and formaldehyde in the reactions of Cl with VA and AA, respectively, are at odds with currently accepted mechanistic pathways.

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### Introduction

In addition to emissions from natural sources (vegetation and biomass combustion) industrial activities have resulted in the wide-spread release of acetates to the atmosphere.<sup>1</sup> Emissions from automobiles represent another source of these compounds; a number of acetates, including vinyl acetate (VA: CH<sub>3</sub>C(O)OCH=CH<sub>2</sub>) and allyl acetate (AA: CH<sub>3</sub>C(O)OCH<sub>2</sub>CH=CH<sub>2</sub>), have been detected as products in the combustion of rape methyl esters used as fuel alternatives or additives.<sup>2</sup>

The gas-phase removal processes of these esters from the atmosphere, and volatile organic compounds (VOCs) in general, is mainly through their reactions with OH, NO<sub>3</sub>, and O<sub>3</sub> with removal by Cl being thought to play, under most circumstances, a very minor role since the global Cl atom concentration is low (<10<sup>3</sup> radicals cm<sup>-3</sup>).<sup>3-5</sup> The general conception has been that

any significant removal of VOCs through reaction with Cl atoms is constrained to (i) the marine boundary layer and coastal regions,<sup>6,7</sup> and (ii) industrial areas where chlorine can be emitted directly from incineration and power generation.<sup>8,9</sup> However, a series of recent observations of nitryl chloride (ClNO<sub>2</sub>) in marine and mid-continental air<sup>10,11</sup> and in urban power plants plumes<sup>12</sup> have highlighted the potential importance of ClNO<sub>2</sub> as a hitherto unconsidered source of Cl and indicated that the role of Cl atoms in initiating the oxidation of VOCs may be more widespread and significant than previously thought. Nitryl chloride is formed during the night *via* the heterogeneous reaction of N<sub>2</sub>O<sub>5</sub> with particle Cl<sup>-</sup> and photolyzes readily in the early morning to produce Cl and an NO<sub>2</sub> molecule.<sup>13</sup> A field and modelling study of Cl<sub>2</sub> and ClNO<sub>2</sub> in the coastal marine boundary layer has recently been reported for the Los Angeles region.<sup>14</sup> The results indicated that over the course of an entire model day ClNO<sub>2</sub> accounted for 45% of the integrated Cl-atom production compared to only 10% for Cl<sub>2</sub> with the remaining 45% being attributed to the reaction of OH with HCl. The study also showed that Cl-atom mediated chemistry could contribute quite substantially to the photooxidation of VOCs in this region particularly in the early morning.

In order, to evaluate the contribution of VA and AA to the oxidative capacity of the atmosphere and potential environmental and health effects detailed kinetic and mechanistic information on their tropospheric gas-phase degradation pathways are required. There have been several kinetic studies of the reactions of VA and AA with OH,<sup>15-17</sup> NO<sub>3</sub>,<sup>17</sup> O<sub>3</sub> (ref. 17)

<sup>a</sup>Instituto de Investigaciones en Físicoquímica de Córdoba (I.N.F.I.Q.C.), Dpto. de Físicoquímica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba. Ciudad Universitaria, 5000 Córdoba, Argentina. E-mail: mteruel@fcq.unc.edu.ar; Fax: +54 351 4334188; Tel: +54 351 5353866 int. 53531

<sup>b</sup>Physikalische & Theoretische Chemie/FBC, Bergische Universitaet Wuppertal, Wuppertal, Germany. E-mail: barnes@uni-wuppertal.de; Fax: +49 202 439 2505; Tel: +49 202 439 2510

<sup>c</sup>"Al. I. Cuza" University of Iasi, Faculty of Inorganic and Analytical Chemistry, Iasi, Romania

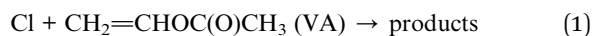
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and Cl.<sup>18</sup> In addition, product studies on the OH-radical initiated oxidation of these unsaturated esters have also been reported. Picquet-Varrault *et al.* have reported product studies on the reactions of OH radicals with both VA<sup>17</sup> and AA<sup>19</sup> performed at atmospheric pressure and room temperature in the presence of NO<sub>x</sub> using FTIR spectrometry for the analyses. Picquet-Varrault *et al.*<sup>17</sup> reported formaldehyde, formic acetic anhydride and acetic acid as the main products formed in the reaction of OH with VA. For the reaction of OH with AA acetoxyacetaldehyde and HCHO were the main products observed.<sup>19</sup>

We have recently reported room temperature product investigations on the gas-phase reactions of OH radicals with VA and AA in the presence and absence of NO<sub>x</sub>.<sup>20</sup> Our results in the presence of NO<sub>x</sub> agreed well with those reported by Picquet-Varrault *et al.*<sup>17–19</sup> for the two compounds. However, our studies showed that in the absence of NO<sub>x</sub> there are significant changes in the relative importance of the possible product channels for the reaction of the 1,2-hydroxyalkoxy radicals formed after addition of OH to the double bond in the compounds. In the case of VA, an  $\alpha$ -ester rearrangement to produce CH<sub>3</sub>C(O)OH and CH<sub>2</sub>(OH)CO' radicals rather than decomposition to form formic acetic anhydride dominated. In the case of AA reaction of the 1,2-hydroxyalkoxy radical with O<sub>2</sub> to form the carbon chain-retaining product 3-hydroxy-2-oxo-propyl ester (CH<sub>3</sub>C(O)OCH<sub>2</sub>C(O)CH<sub>2</sub>OH) dominated in the absence of NO<sub>x</sub> contrasting very sharply with the decomposition channel of the 1,2-hydroxyalkoxy radicals to form acetoxyacetaldehyde and HCHO, which dominated when the reaction was studied in the presence of NO<sub>x</sub>.

In a continuation of our investigations on the photooxidation mechanisms of unsaturated VOCs for different NO<sub>x</sub> scenarios, we report here product studies on the Cl-atom initiated photooxidation of VA and AA in the presence and absence of NO<sub>x</sub>:



A computational study on the mechanism and kinetics of the Cl-initiated oxidation of VA in the presence of NO<sub>x</sub> was reported recently.<sup>21</sup> The study found that Cl addition to the double bond is the dominate pathway followed, in the presence of O<sub>2</sub> and NO, by decomposition to give the major products observed in our work.

To the best of our knowledge this is the first reported experimental product investigation of the Cl-atom initiated photooxidation for both VA and AA performed in the presence and in the absence of NO<sub>x</sub>.

## Experimental section

All the experiments were performed in a 1080 L quartz-glass reaction chamber at (298 ± 2) K and a total pressure of (760 ± 10) Torr of synthetic air (760 Torr = 101.325 kPa). A detailed description of the reactor can be found elsewhere<sup>22</sup> and

only a brief description is given here. The photolysis system consists of 32 superactinic fluorescent lamps (Philips TL05 40W: 320–480 nm,  $\lambda_{\text{max}} = 360$  nm), which are spaced evenly around the reaction vessel. The chamber is equipped with a White type multiple-reflection mirror system with a base length of (5.91 ± 0.01) m for sensitive *in situ* long path infrared absorption monitoring of reactants and products in the spectral range 4000–700 cm<sup>-1</sup>. The White system was operated at 82 traverses, giving a total optical path length of (484.7 ± 0.8) m. Infrared spectra were recorded with a spectral resolution of 1 cm<sup>-1</sup> using a Nicolet Nexus FT-IR spectrometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT) detector.

Chlorine atoms were generated by the photolysis of Cl<sub>2</sub> using the fluorescent lamps:



Experiments were performed on mixtures of Cl<sub>2</sub>/acetate/air or Cl<sub>2</sub>/acetate/NO/air which were irradiated for periods up to 5 minutes during the course of which infrared spectra were recorded at 1 cm<sup>-1</sup> resolution with the FTIR spectrometer. Tests showed that photolytic removal of the acetates in the absence of Cl<sub>2</sub> and NO was negligible. The systems, in particular the AA system, are very reactive and typically 20 interferograms were co-added per spectrum over a period of approximately 5 min for the experiments with VA and 10 interferograms for the experiments with AA. The concentrations of the reactants used in the experiments and the infrared frequencies used for monitoring are given in the ESI.†

The quantification of reactants and products was performed by comparison with calibrated reference spectra contained in the IR spectral data bases of the laboratories in Wuppertal and Laboratoire Interuniversitaire des Systemes Atmosphériques (LISA), Paris, France.<sup>23</sup>

## Results

### Cl + vinyl acetate

**NO<sub>x</sub>-containing system.** A typical product spectrum obtained after irradiation of a VA/Cl<sub>2</sub>/air/NO mixture and subtraction of residual absorptions due to VA is shown in Fig. 1, panel A. Infrared spectra of formic acetic anhydride, formyl chloride, acetic acid, and carbon monoxide are shown in Fig. 1, panels B, C, D and E, respectively. After subtraction of absorptions from these identified products absorptions remain at 786, 853, 1193, 1322, 1698, 1801 and 3588 cm<sup>-1</sup> as shown in Fig. 1, panel F. The residual absorptions are due mainly to nitrosyl chloride (ClNO) and nitryl chloride (ClNO<sub>2</sub>) formed from the reactions of Cl atoms with NO and NO<sub>2</sub>, respectively, and also some nitric acid (HNO<sub>3</sub>) formed through reaction of OH with NO<sub>2</sub> and heterogeneous reactions of NO<sub>x</sub> at the reactor wall. The reactions of NO with the HO<sub>2</sub> radicals formed in the system will produce OH radicals, however, since the rate coefficients for Cl with VA is nearly an order of magnitude higher than the corresponding OH reaction and OH is scavenged by NO<sub>2</sub>, interference by OH



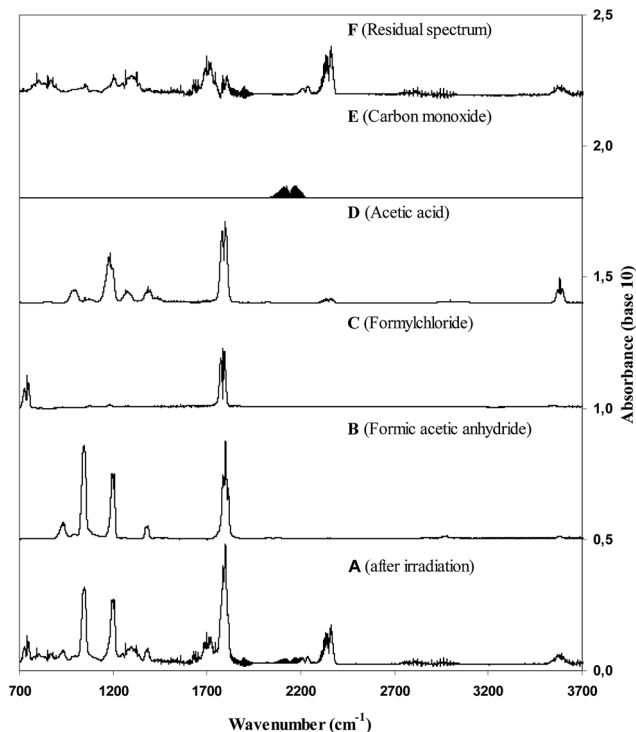


Fig. 1 Panel A shows the product spectrum obtained from the irradiation of a VA/Cl<sub>2</sub>/NO<sub>x</sub>/air reaction mixture. Panels B, C, D and E show reference spectra of formic acetic anhydride, formyl chloride, acetic acid, and carbon monoxide, respectively. Panel F shows the residual product spectrum obtained after the subtraction of the identified products.

chemistry will be minimal. This also applies to the AA reaction system in the presence of NO<sub>x</sub>.

Concentration–time profiles of VA and the identified products, formic acetic anhydride, formyl chloride, acetic acid and carbon monoxide are shown in Fig. S1 of the ESI.† Plots of the concentrations of the identified products as a function of

reacted VA are shown in Fig. S2.† As can be seen in Fig. S1† the increase in the product concentrations scale linearly with the loss of VA supporting that the products are all primary and that secondary loss or formation of these products is insignificant. The molar yields of the products observed in the reaction of Cl with VA in the presence of NO<sub>x</sub>, obtained from the slopes of the plots in Fig. S2,† are listed in Table 1.

**NO<sub>x</sub>-free system.** Fig. S3, panel A in the ESI,† shows the IR spectrum obtained after UV irradiation of a VA/Cl<sub>2</sub>/air mixture and subtraction of residual absorptions due to VA. Fig. S3,† panels B, C, D, and E show reference spectra of formic acetic anhydride, formyl chloride, acetic acid and carbon monoxide, respectively, all of which have been identified as products. Fig. S3,† panel F shows the residual spectrum that is obtained after subtraction of absorptions from the identified products from the spectrum in panel A; unidentified absorptions remain at approximately 1017, 1059, 1111, 1205, 1372 and 1808 cm<sup>-1</sup>.

Many of the absorption features in the residual product spectrum correlate very well with those of acetic acid anhydride and chloroacetone indicating that the compound (or compounds) giving rise to the IR features contains structural elements common to both acetic acid anhydride and chloroacetone. Since we are certain that all other possible reaction products from the reaction of Cl with VA have been accounted for we are confident that the unidentified absorptions are mainly due to the formation of the VA carbon-skeleton retaining compound chloro-acetic acid anhydride (CH<sub>3</sub>C(O)OC(O)CH<sub>2</sub>Cl) although contributions from CH<sub>3</sub>C(O)OC(OH)CH<sub>2</sub>Cl can not be excluded. Further justification for the formation of CH<sub>3</sub>C(O)OC(O)CH<sub>2</sub>Cl from the 1,2-chloroalkoxy radicals formed in the Cl + vinyl acetate reaction are given in the discussion on the formation of CH<sub>3</sub>C(O)OCH<sub>2</sub>C(O)CH<sub>2</sub>Cl in the reaction of Cl with allyl acetate.

Concentration–time profiles of VA and the four identified products are shown in the ESI in Fig. S4.† Plots of the concentrations of the products as a function of reacted VA for the NO<sub>x</sub>-free reaction system are shown in Fig. 2. The plots are

Table 1 Formation yields of the oxidation products identified from the Cl atom oxidation of vinyl and allyl acetate studied in the presence and the absence of NO<sub>x</sub>. The quoted errors are the 2σ statistical errors from the linear regression analyses

Acetate	Product	Yield (%) (NO <sub>x</sub> - containing)	Yield (%) (NO <sub>x</sub> - free)
CH <sub>3</sub> C(O)OCH=CH <sub>2</sub> (vinyl acetate)	CH <sub>3</sub> C(O)OC(O)H (formic acetic anhydride)	69 ± 8	25 ± 5
	CH <sub>3</sub> C(O)OC(O)CH <sub>2</sub> Cl	—	~50 <sup>a</sup>
	CH <sub>3</sub> C(O)OH	27 ± 5	12 ± 3
	HC(O)Cl	94 ± 12	48 ± 8
	HC(O)H	≤5	—
	CO	30 ± 5	15 ± 4
	CH <sub>3</sub> C(O)OCH <sub>2</sub> CH=CH <sub>2</sub> (allyl acetate)	CH <sub>3</sub> C(O)OCH <sub>2</sub> C(O)H (acetoxyacetaldehyde)	66 ± 8 <sup>a</sup>
CH <sub>3</sub> C(O)OCH <sub>2</sub> C(O)CH <sub>2</sub> Cl		≤5	≥95 <sup>b</sup>
CH <sub>3</sub> C(O)OC(O)H (formic acetic anhydride)		Secondary	≤5
CH <sub>3</sub> C(O)OH		Secondary	≤5
HC(O)Cl		Secondary	≤5
HC(O)H		>90	≤5
CO		Secondary	≤5

<sup>a</sup> Lower limit observations; attempted corrections for secondary consumption support a much higher yield (see text). <sup>b</sup> Estimate based on experimental observations.



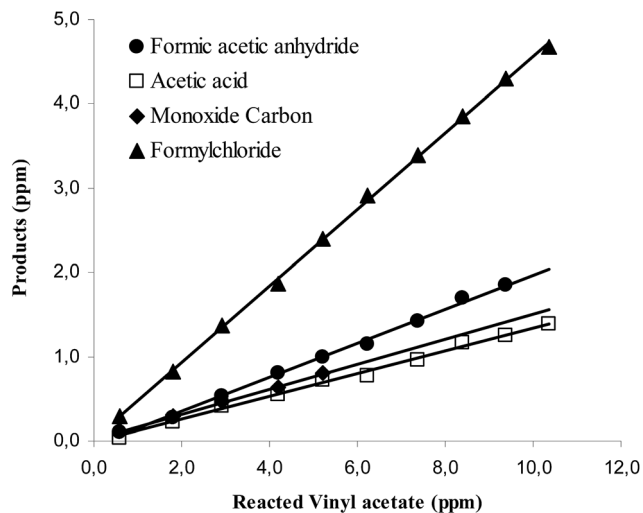


Fig. 2 Plot of the concentrations of the products formed in the reaction of Cl with VA in the absence of NO as a function of the amount of reacted VA.

linear with near zero intercepts supporting that the products are all primary. The molar yields of the products observed in the reaction of Cl with VA in the absence of  $\text{NO}_x$ , obtained from the slopes of the plots in Fig. 2, are listed in Table 1.

#### Cl + allyl acetate

**$\text{NO}_x$ -containing system.** Panel A of Fig. S5 in the ESI† shows a typical product spectrum acquired after irradiation of a AA/ $\text{Cl}_2$ /air/ $\text{NO}$  mixture and subtraction of residual absorptions due to AA. Panels B, C, D, E and F show the reference spectrum of formic acetic anhydride, formyl chloride, acetic acid, formaldehyde and acetoxyacetaldehyde ( $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{H}$ ), respectively. These compounds have been identified as products in the reaction system along with CO, the absorptions of which can be seen around  $2200\text{ cm}^{-1}$  in Fig. S5,† panel A. Panel G shows the residual spectrum obtained after the subtraction of absorptions due to the identified products. In the residual spectra many absorption bands remain in the fingerprint region and in the region  $1671\text{--}1808\text{ cm}^{-1}$ . As in the VA system with  $\text{NO}_x$  some of these absorptions can be assigned unequivocally to nitrosyl chloride, nitryl chloride and nitric acid. In addition, to these compounds, as will be argued in the Discussion, bands at  $1744$ ,  $1300$ ,  $1047$  and  $795\text{ cm}^{-1}$  are assigned to formation of acetoxyacetyl peroxyxynitrate ( $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{OONO}_2$ ).

Fig. S6† shows the concentration–time profiles of AA and the identified products formed in the  $\text{NO}_x$ -containing system. The profile of AA shows that it is being consumed very rapidly in the system. The initial concentration–time profiles of acetoxyacetaldehyde and HCHO are similar and indicate that they are both primary products. However, secondary removal of acetoxyacetaldehyde and especially HCHO in secondary reactions with Cl is clearly evident.

Although the concentration–time profiles of acetic acid, formic acetic anhydride and CO look as though they may be

primary products, plots of their concentrations against the amount of AA consumed have non-zero intercepts and upward curvature which increases with increasing reaction time (see Fig. S7 in the ESI†). This behavior is indicative of formation of these compounds in secondary reactions. The formation of acetic acid and formic acetic anhydride in the system is attributed to fast secondary reactions of acetoxyacetaldehyde with Cl (see Discussion). Formation of formyl chloride was also observed in the system; however, it was only observed in small quantities toward the end of the reaction and is obviously being formed in secondary reactions.

The initial slopes of the plots of the concentrations of acetoxyacetaldehyde and HCHO against reacted AA indicate high yields for both compounds. Taking the first few points of a plot of the concentration of acetoxyacetaldehyde as a function of reacted AA gives a yield of acetoxyacetaldehyde of close to unity, however, if all the points are taken a yield of around 66% is obtained caused by curvature in the plot from fast secondary reaction of acetoxyacetaldehyde with Cl. Correction of yield for formaldehyde for secondary consumption with Cl using the method outlined in Tuazon *et al.*<sup>24</sup> and a rate coefficient of  $7.32 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  for the reaction of Cl with HCHO<sup>25</sup> gives a yield of >90% for HCHO. The rate coefficient for the reaction of Cl with acetoxyacetaldehyde is not known. Using the rate coefficient for Cl with HCHO for the correction gave a yield of around 120%. Since the rate coefficient for Cl with acetoxyacetaldehyde is not likely to be much less than that for Cl with HCHO this would support a yield much higher than 66% yield for acetoxyacetaldehyde.

**$\text{NO}_x$ -free system.** The irradiation of a AA/ $\text{Cl}_2$ /air mixture give rise to the product spectrum shown in Fig. S8,† panel A. Formation of minor amounts of acetoxyacetaldehyde, formic acetic anhydride, acetic acid and formaldehyde were observed but the molar yields for each of these products was <5% (Table 1). Reference spectra of chloroacetone and methyl acetate are shown in Fig. S8,† panels B and C, respectively. It can be seen that the product spectrum in Fig. S8,† panel A, contains absorption features that match those in both the spectrum of methyl acetate and that of chloroacetone. In fact, when these two spectra are mathematically added the resulting spectrum almost completely matches all of the features in the residual product spectrum supporting that the compound must contain the  $\text{CH}_3\text{C}(\text{O})\text{O}$ - and  $-\text{COCH}_2\text{Cl}$  entities. Since addition of Cl will be predominately at the terminal carbon of the double bond and the yields of carbon cleavage products are minimal we are quite confident that the absorptions in the IR spectrum in Fig. S8,† panel A, are predominantly due to the formation of acetic acid 3-chloro-2-oxo-propyl ester ( $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{C}(\text{O})\text{CH}_2\text{Cl}$ ). Formation of  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{Cl})\text{C}(\text{O})\text{H}$  and other hydroperoxy and hydroxyl compounds from peroxy-peroxy reactions in the system are obviously also possible, however, based on the observed infrared product spectra, we estimate that the yields of these compounds must be very low. For example,  $\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{CH}(\text{Cl})\text{C}(\text{O})\text{H}$  would not give rise to the strong absorptions observed at around  $1245$  and  $1050\text{ cm}^{-1}$ . Formation of the compound would also not be in line with the high observed yield of acetoxyacetaldehyde in the



$\text{NO}_x$ -containing system. It is well established that a major channel in the reactions of the 1,2-chloroalkoxy radicals formed in the addition of Cl to alkenes is reaction of the 1,2-chloroalkoxy radicals with  $\text{O}_2$  to form a 1,2-chloro carbonyl compound,<sup>26</sup> for example, Butt *et al.* (2009)<sup>27</sup> have observed carbon-skeleton retaining compound  $\text{C}_4\text{F}_9\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{C}(\text{O})\text{CH}_2\text{Cl}$  as a major product from the addition of Cl to 4 : 2 fluorotelomer acrylate ( $\text{C}_4\text{F}_9\text{CH}_2\text{CH}_2\text{OC}(\text{O})\text{CH}=\text{CH}_2$ ) both in the presence and absence of  $\text{NO}_x$ .

Further support comes from recent work on long chain  $\text{C}_x$  to  $\text{C}_9$  terminal alkenes by Walavalkar *et al.*<sup>28</sup> which showed that addition of Cl to the inner carbon of the double bond is minimal and that 1-chloro-2-ketones are the main products in the absence of  $\text{NO}_x$ . The above points serve to strengthen the arguments offered for the identification of acetic acid 3-chloro-2-oxo-propyl ester as the main product in the reaction of Cl with allyl acetate in the absence of NO.

The near quantitative formation of acetic acid 3-chloro-2-oxo-propyl ester in the reaction of Cl with AA in the absence of  $\text{NO}_x$  allows an approximate IR calibration of the compound. Using the band at  $3415\text{ cm}^{-1}$  which is unique to the compound allows a yield of  $\leq 5\%$  to be placed on the formation of the ester in the reaction of Cl with AA in the presence of  $\text{NO}_x$ .

## Discussion

### Cl + vinyl acetate

**Reaction with  $\text{NO}_x$ .** As can be deduced from Table 1 the carbon balance for the reaction of Cl with VA in the presence of  $\text{NO}_x$  is, within the error limits, approximately 100%. The reaction will proceed *via* addition of Cl to the double bond followed by consecutive addition of  $\text{O}_2$  and reaction with NO form  $\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{O}^\cdot)\text{CH}_2\text{Cl}$  alkoxy radicals (Fig. 3, channel A). Three channels are traditionally thought be operative for the radicals, decomposition, an  $\alpha$ -ester rearrangement and reaction with  $\text{O}_2$ , Fig. 3, channels B, C and D, respectively. The later channel is not observed with NO. Decomposition to form formic acetic anhydride with a yield of  $(69 \pm 8)\%$  is observed. The expected co-product is the  $\text{Cl}-\text{CH}_2^\cdot$  radical which would be expected to add  $\text{O}_2$  giving peroxy radicals which react further with NO to form  $\text{Cl}-\text{CH}_2\text{O}^\cdot$  alkoxy radicals. Further reaction of these radicals with  $\text{O}_2$  are a potential pathway to the formation of  $\text{HC}(\text{O})\text{Cl}$  detected in the system.

However, Bilde *et al.*<sup>29</sup> have studied the reaction of  $\text{Cl}-\text{CH}_2^\cdot$  radicals in  $\text{N}_2$  with different partial pressures of  $\text{O}_2$  in the presence and absence of  $\text{NO}_x$ . They produced the radicals *via* reaction of Cl with  $\text{CH}_3\text{Cl}$ . They did not measure the decay of  $\text{CH}_3\text{Cl}$  since this was too small and determined the product

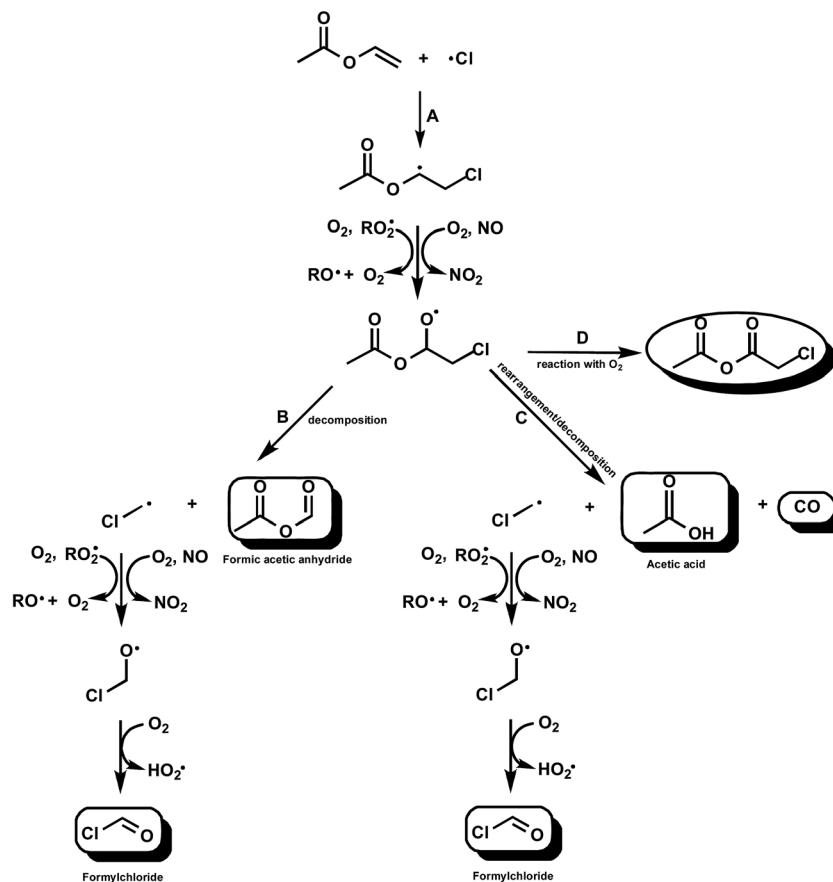


Fig. 3 Simplified mechanism for the Cl-atom initiated oxidation of VA ( $\text{CH}_2=\text{CHOC}(\text{O})\text{CH}_3$ ) *via* addition of Cl to the terminal carbon of the double bond.





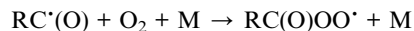
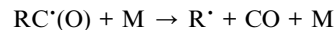
yields from the sum of the three identified carbon-containing products HCOCl, HCHO and CO which they assumed was equal the amount of consumed CH<sub>3</sub>Cl. They found that in the absence of NO<sub>x</sub> the final product was HC(O)H in nearly 100% yield and that with NO<sub>x</sub> in 700 Torr of air HC(O)Cl, HC(O)H and CO were products with yields of (56 ± 10), (32 ± 6) and (12 ± 5)%, respectively. The result of Bilde *et al.* with NO<sub>x</sub> contrasts sharply with the large yield of HC(O)Cl and no HC(O)H observed in the reaction of Cl with VA in the presence of NO<sub>x</sub> presented here. Bilde *et al.*<sup>29</sup> attributed the differences in the yields of HC(O)Cl with and without NO<sub>x</sub> to the formation of excited Cl-CH<sub>2</sub>O\* alkoxy radicals in the exothermic reaction of Cl-CH<sub>2</sub>OO' peroxy radicals with NO<sub>x</sub> whereas in the NO<sub>x</sub>-free system only thermalized Cl-CH<sub>2</sub>O' radicals are formed through nearly thermo neutral peroxy-peroxy reactions.

At present it is difficult to explain why we observe mainly formation of HC(O)Cl from the reactions of the Cl-CH<sub>2</sub>' radical formed in the reaction of Cl with VA in the presence of NO<sub>x</sub> in contrast to the findings of Bilde *et al.*<sup>29</sup> The situation is made even more curious by the fact that in the Cl/AA/NO/air system we observe HC(O)H as the co-product of acetoxyacetaldehyde and not HC(O)Cl. One obvious difference is the source of the Cl-CH<sub>2</sub>' radicals in the studies. Our observations imply that the decomposition channel is not as straightforward as depicted in Fig. 3, *i.e.* the mechanism is much more complex and may not involve formation of Cl-CH<sub>2</sub>' radicals.

The only structural difference between vinyl acetate and allyl acetate is the -CH<sub>2</sub>- group in allyl acetate between the oxygen atom and the double bond. This difference in structure is apparently critical in determining the reaction products resulting from the terminal -CH<sub>2</sub>Cl group after consecutive addition of Cl and O<sub>2</sub> to form 1,2-chloroperoxy radicals. The carbonyl and C-Cl entities in the intermediate 1,2-chloroperoxy radical reaction intermediates are strongly electron withdrawing. It is possible that there are bonding interactions between the peroxy radicals and the carbonyl and C-Cl entities in the reaction intermediates which complicate the reactions of NO and probably also HO<sub>2</sub>/RO<sub>2</sub> radicals with the 1,2-chloroperoxy radical intermediates and thus the reaction pathways and products. The 1,2-chloroperoxy radical formed in the reaction of Cl with allyl acetate could form a weakly bound six-membered ring with the carbonyl group which would be more favorable than a five-membered ring which could be formed in the reaction of Cl with vinyl acetate. Interaction of the peroxy group with C-Cl and NO could potentially result in the product of chemically activated CH<sub>2</sub>ClO radicals especially in the case of vinyl acetate where interaction of the peroxy group with the carbonyl group is probably not as important as for allyl acetate. This is presently purely speculation and obviously more detailed laboratory studies as a function of temperature, pressure and O<sub>2</sub> and in particular computational studies are needed to shed light on the mechanistic differences observed in the reactions of Cl with vinyl acetate and allyl acetate in the presence and absence of NO.

The other important channel in the reaction of Cl with VA involves an ester rearrangement<sup>30</sup> to form CH<sub>3</sub>C(O)OH with a yield of (27 ± 5)% and the halogenated acyl radical Cl-CH<sub>2</sub>C'(O).

There are two known fates of acyl radicals either thermal decomposition or addition of O<sub>2</sub> to form acylperoxy radicals:<sup>31-34</sup>



For acyl radicals addition of O<sub>2</sub> at atmospheric pressure and room temperature is known to dominate,<sup>33,34</sup> however, there is a known monotonic trend towards decomposition, at 298 K and atmospheric pressure of air, with increase in the number of Cl in the CCl<sub>x</sub>F<sub>3-x</sub>C'(O) radical.<sup>28,29</sup> Although a theoretical study on the atmospheric fate of carbonyl radicals predicts that the main fate of the Cl-CH<sub>2</sub>C'(O) radical is addition of O<sub>2</sub> and not decomposition the experimental observations in this study of primary CO formation suggests rapid decomposition of the Cl-CH<sub>2</sub>C'(O) radical into CO and a Cl-CH<sub>2</sub>' radical rather than addition of O<sub>2</sub> (Fig. 3, channel C).

If addition of O<sub>2</sub> to Cl-CH<sub>2</sub>C'(O) was an important channel the peroxy radicals formed would, due to the high NO<sub>2</sub> levels, add NO<sub>2</sub> to a significant extent to form the thermally stable PAN type compound ClCH<sub>2</sub>C(O)OONO<sub>2</sub>. No evidence could be found in the product spectra for the formation of a PAN type compound.

During this writing a computational study on the mechanism and kinetics of the Cl-initiated oxidation of VA appeared.<sup>21</sup> The study found that H-atom abstraction pathways were negligible and that Cl addition dominated followed, in the presence of O<sub>2</sub> and NO, by decomposition to give CH<sub>3</sub>C(O)OC(O)H, CH<sub>3</sub>C(O)OH and HC(O)Cl as major products as observed in this work. The product channels observed for the reaction of Cl with VA in the presence of NO<sub>x</sub> are similar to those observed in the analogous OH reaction,<sup>20</sup> however, with a higher preference for the channel forming CH<sub>3</sub>C(O)OC(O)H in the OH reaction.

**Reaction without NO<sub>x</sub>.** In Fig. 3 the peroxy radicals formed after reaction of Cl with VA are shown to form wholly alkoxy radicals *via* reaction with HO<sub>2</sub> or other peroxy radicals. Other pathways are known to form a hydroperoxy or alcohol, however, the yields of detected products and residual IR product spectra suggest that these are relatively minor channels for both the VA and AA systems. In the absence of NO<sub>x</sub>, the two decomposition channels producing CH<sub>3</sub>C(O)OC(O)H and HCOCl (Fig. 3, channel B) and the ester rearrangement producing CH<sub>3</sub>C(O)OH, CO and HCOCl (Fig. 3, channel C) are observed for the CH<sub>3</sub>C(O)OCH(O')CH<sub>2</sub>Cl radicals formed in the reaction of Cl with VA. However, compared to the system with NO<sub>x</sub> the relative contributions of these channels to the overall reaction are much reduced with the channels B and C accounting for only (25 ± 5) and (12 ± 3)% of the overall reaction, respectively. The combined yield of HC(O)Cl from these two channels was (48 ± 8)%.

The results clearly show that in the absence of NO<sub>x</sub>, only approximately 50% of the reaction is proceeding by the decomposition and rearrangement/decomposition channels of the chloroalkoxy radicals (Fig. 3, channels B and C). As indicated in the Results section the experimental observations support the occurrence of a molecular channel with the formation of chloro-acetic acid anhydride (CH<sub>3</sub>C(O)OC(O)



CH<sub>2</sub>Cl) through the reaction of the CH<sub>3</sub>C(O)OCH(O<sup>•</sup>)CH<sub>2</sub>Cl with O<sub>2</sub> (Fig. 3, channel D). Based on the carbon balance the yield of chloro-acetic acid anhydride could be potentially as high as 50%. Unfortunately no calibrated reference spectrum is available to verify this.

This result for the reaction of Cl with VA in the absence of NO<sub>x</sub> contrasts quite markedly with that for the analogous OH reaction under the same conditions. For the reaction of OH with VA in the absence of NO<sub>x</sub> a molecular channel is not observed. The absence of NO<sub>x</sub> just results in a stark switch in the preference of the two decomposition channels, *i.e.* the ester rearrangement channel dominates in the absence of NO<sub>x</sub> compared to a dominance of the anhydride forming channel in the presence of NO<sub>x</sub>.<sup>20</sup> The substantially lower yields of primary decomposition products for the reaction of Cl with VA in the absence of NO<sub>x</sub> suggests that chemical activation is important in the atmospheric chemistry of CH<sub>3</sub>C(O)OCH(O<sup>•</sup>)CH<sub>2</sub>Cl alkoxy radicals.

### Cl + allyl acetate

**Reaction with NO<sub>x</sub>.** In this reaction system Cl adds mainly to the terminal carbon of the double bond in AA followed by the addition of O<sub>2</sub> to give peroxy radicals which subsequently react with NO to form 1,2-chloroalkoxy radicals as shown in Fig. 4, channel A. Possible reaction channels include decomposition to form acetoxyacetaldehyde and CH<sub>2</sub>Cl radicals (channel B), decomposition to form chloroacetaldehyde and CH<sub>3</sub>C(O)OCH<sub>2</sub>

radicals (channel C) or reaction with O<sub>2</sub> to form the chain-retaining product CH<sub>3</sub>C(O)OCH<sub>2</sub>C(O)CH<sub>2</sub>Cl (Fig. 4, channel D).

There was no indication for formation of chloroacetaldehyde in the product spectrum showing that channel C is a negligible reaction pathway. As discussed below, from the study on the reaction of Cl with AA in the absence of NO<sub>x</sub> we are able to put a yield of ≤5% on the formation of CH<sub>3</sub>C(O)OCH<sub>2</sub>C(O)CH<sub>2</sub>Cl from the reaction of the 1,2-chloroalkoxy radicals with O<sub>2</sub> (channel D) in the presence of NO<sub>x</sub>.

In the product study with NO<sub>x</sub>, acetoxyacetaldehyde, and formaldehyde have been identified as major primary products. The results indicate that the major reaction channel after addition of is cleavage of the C–C bond to form acetoxyacetaldehyde and potentially CH<sub>2</sub>Cl<sup>•</sup> radicals (Fig. 4, channel B).

As discussed in the Results section although a lower limit of 66% is given in Table 1 for the yield of acetoxyacetaldehyde the observations would suggest that after correction it would be close to unity.

In stark contrast to the reaction of Cl with VA in the presence of NO, HC(O)H is detected as the main co-product originating from the decomposition channel and not HC(O)Cl. As in the VA/Cl/NO/air system, based on the study of Bilde *et al.*,<sup>29</sup> this observation is again in strong contrast to what would be expected from further reactions of the ClCH<sub>2</sub><sup>•</sup> radical in the presence of NO. As discussed in the section on the reaction of Cl with NO the decomposition channel as shown in Fig. 4 for the reaction of Cl with AA would appear to be much more complex.

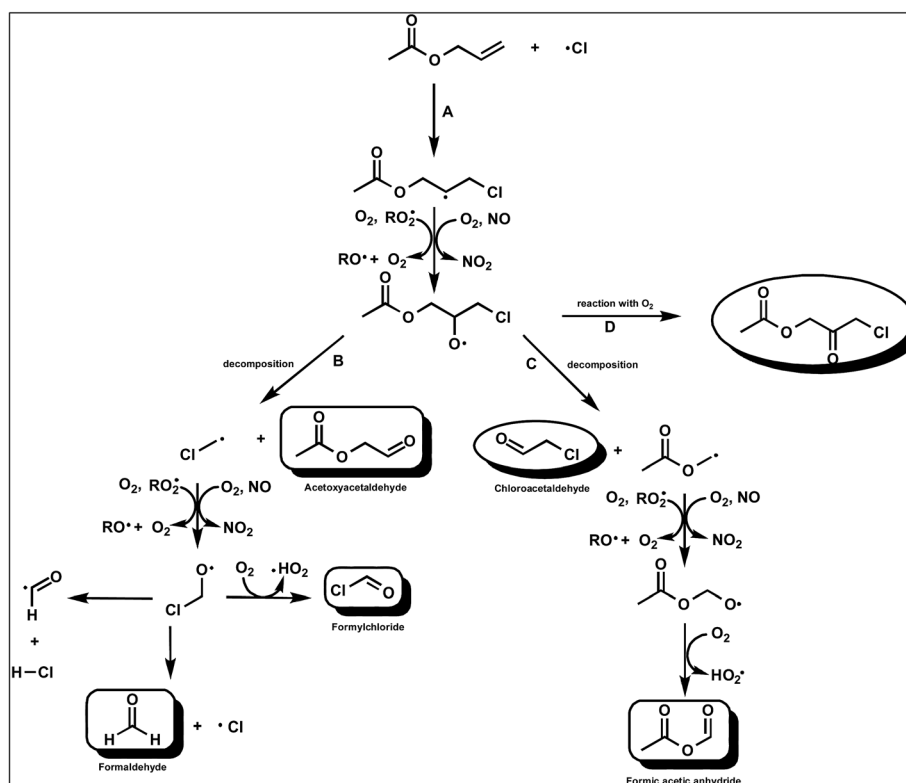
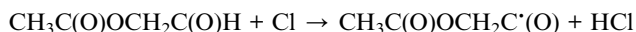


Fig. 4 Simplified mechanism for the Cl-atom initiated oxidation of AA (CH<sub>2</sub>=CHCH<sub>2</sub>OC(O)CH<sub>3</sub>) via addition of Cl to the terminal carbon of the double bond.

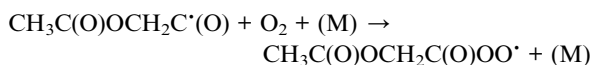


Insertion of a  $-\text{CH}_2-$  group between the acetoxy and double bond of VA and AA has resulted in the chlorinated terminal carbon of the compounds producing  $\text{HC(O)Cl}$  in the case of VA and  $\text{HC(O)H}$  in the case of AA. The classically accepted mechanism involving C–C cleavage to form  $\text{CH}_2\text{Cl}^\bullet$  radicals can not explain the present product observations in the VA and AA reaction systems.

In addition, to the fast secondary reaction of HCHO in the reaction system, there is obviously also considerable secondary reaction of acetoxyacetaldehyde with Cl. This reaction will proceed mainly through H-atom abstraction from the aldehydic hydrogen:

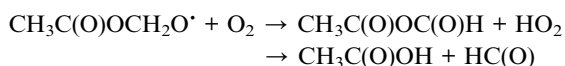


The resulting acyl radicals are expected, under the experimental conditions, to predominantly add  $\text{O}_2$  to form peroxy radicals rather than decompose:



In the reaction system the peroxy radicals can react with NO or add  $\text{NO}_2$ . Reaction with NO will result mainly in the formation of  $\text{RC(O)O}^\bullet$  radicals which lose  $\text{CO}_2$  and form  $\text{CH}_3\text{C(O)OCH}_2^\bullet$  radicals. These radicals undergo further consecutive reactions with  $\text{O}_2$  and NO to give  $\text{CH}_3\text{C(O)OCH}_2\text{O}^\bullet$  radicals.

There are two possible reaction pathways for the  $\text{CH}_3\text{C(O)OCH}_2\text{O}^\bullet$  radical either reaction with  $\text{O}_2$  to form formic acetic anhydride or an  $\alpha$ -ester rearrangement to form acetic acid and  $\text{HC(O)}$  radicals.



Both acetic acid and formic acetic anhydride have been detected as products in the Cl + AA reaction system in the presence of  $\text{NO}_x$ . We attribute the formation of both of these compounds to secondary reactions of acetoxyacetaldehyde with Cl though the sequence of reactions outlined above. The ratio of the yield of acetic acid to formic acetic anhydride is approximately 4 : 1 and remains fairly constant throughout the reaction. Picquet-Varrault *et al.*<sup>35</sup> have obtained yields of 75 and 15 for the formation of acetic acid and acetoxyacetaldehyde in the reaction of OH with ethyl acetate which also involves an  $\alpha$ -ester rearrangement. The ratio of the two products is quite similar to that obtained in this study for Cl with acetoxyacetaldehyde and we take this as an additional endorsement that secondary reaction of Cl with acetoxyacetaldehyde is the source of acetic acid and formic acetic anhydride in the Cl + AA reaction system. Picquet-Varrault *et al.*<sup>19</sup> in their study on the reaction of OH with AA found acetoxyacetaldehyde as the main product and strongly suspected that secondary reactions of this compound led to the formation of formic acetic anhydride and acetic acid that they observed in their reaction system. This study supports that the

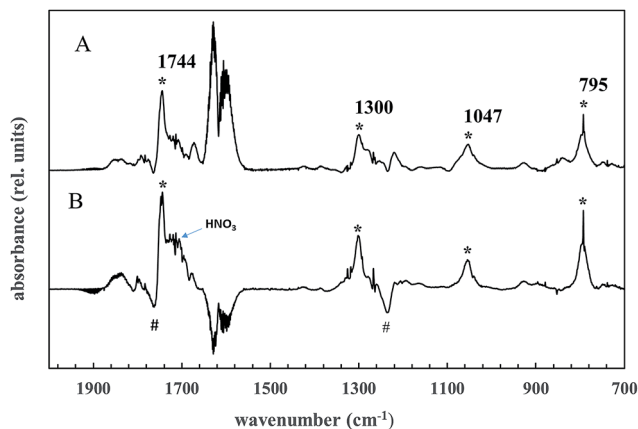
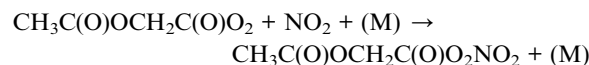


Fig. 5 Trace A shows the spectrum obtained at the end of the irradiation a AA/Cl<sub>2</sub>/NO<sub>x</sub> reaction mixture after subtraction of acetoxyacetaldehyde, acetic acid, formic acetic anhydride and nitric acid. The \* symbols in are attributed to the formation of acetoxyacetyl peroxyxynitrate. Trace B is the difference spectrum obtained after subtraction of the first spectrum in which the AA was zero from the last spectrum in the experiment. This spectrum demonstrates the secondary decay of the main product acetoxyacetaldehyde (# symbols) and the formation of acetoxyacetyl peroxyxynitrate (\* symbols).

reactions of OH and Cl with acetoxyacetaldehyde are similar and result in formation of formic acetic anhydride and acetic acid.

Reaction of the peroxy radicals formed in the reaction of Cl with acetoxyacetaldehyde with  $\text{NO}_2$  will lead to the formation of a peroxyxynitrate.



This type of peroxyxynitrate is expected to be reasonably stable at room temperature and atmospheric pressure.<sup>36,37</sup> Indeed, bands are present in the product spectrum which can be assigned to a peroxyxynitrate. Trace A in Fig. 5 shows the spectrum that is obtained at the end of the irradiation of a AA/Cl<sub>2</sub>/NO<sub>x</sub> reaction mixture after subtraction of acetoxyacetaldehyde, acetic acid, formic acetic anhydride and nitric acid. The \* symbols highlight bands that are characteristic for the formation of a peroxyxynitrate.<sup>36</sup> The band at  $\sim 1744 \text{ cm}^{-1}$  can be assigned to an asymmetric stretching band of  $\text{NO}_2$  (asym.  $\text{NO}_2$ ), that at  $\sim 1330 \text{ cm}^{-1}$  to a symmetrical stretch of  $\text{NO}_2$  (sym.  $\text{NO}_2$ ) and that at  $\sim 795 \text{ cm}^{-1}$  to a  $\text{NO}_2$  deformation. A band at  $\sim 1045 \text{ cm}^{-1}$  is also observed. Bands in this region are observed in the infrared spectra of many peroxyxynitrates, however, we have no vibrational group assignment for this band.

Trace B, Fig. 5 shows a difference spectrum obtained after subtraction of the first spectrum in which the AA concentration was zero from the last spectrum in the experiment. This spectrum shows the continuing secondary decay of the main product acetoxyacetaldehyde (# symbols) and the formation of the bands that we assign to a peroxyxynitrate. The experimental evidence supports that the peroxyxynitrate absorptions are arising predominantly from the formation of thermally stable acetoxyacetyl peroxyxynitrate.





**Reaction without NO<sub>x</sub>.** As discussed in the Results section, the experimental observations support that the fate of the CH<sub>3</sub>C(O)OCH<sub>2</sub>CH(O<sup>•</sup>)CH<sub>2</sub>Cl alkoxy radicals formed in the Cl + AA reaction in the absence of NO<sub>x</sub> is essentially reaction with O<sub>2</sub> to form acetic acid 3-chloro-2-oxo-propyl ester (CH<sub>3</sub>C(O)OCH<sub>2</sub>C(O)CH<sub>2</sub>Cl). The analogous OH reaction in the absence of NO<sub>x</sub> has been observed to form mainly 3-hydroxy-2-oxo-propyl ester (CH<sub>3</sub>C(O)OCH<sub>2</sub>C(O)CH<sub>2</sub>OH)<sup>20</sup> through reaction CH<sub>3</sub>C(O)OCH<sub>2</sub>CH(O<sup>•</sup>)CH<sub>2</sub>OH alkoxy radicals with O<sub>2</sub>, however, a ~26% contribution from the decomposition channel to form acetoxyacetaldehyde and HCHO was also observed.

### Atmospheric implications

As discussed in several publications the main tropospheric chemical removal of unsaturated compounds is reaction with OH radicals and in the case of VA and AA the tropospheric lifetimes respect to degradation through reaction with OH radicals are approximately 3 and 5 h, respectively,<sup>15–20</sup> indicating that these VOCs will be rapidly degraded in the gas phase and near to their emissions sources. The tropospheric lifetimes of the degradation of VA and AA initiated by Cl atoms are 9 and 4 days, respectively.<sup>18</sup> However, in marine and industrialised continental regions, where high chlorine concentrations can occur especially at dawn, Cl– mediated degradation of the compounds may be able to compete with the OH– initiated oxidation. Under high NO<sub>x</sub> conditions both the OH and Cl initiated oxidation of both compounds will give rise to high yields of bond cleavage products including HCHO, HCOCl, CH<sub>3</sub>C(O)OH, formic acetic anhydride and acetoxyacetaldehyde. Further breakdown of acetoxyacetaldehyde will produce more acetic acid and formic acetic anhydride whereby formation of a potentially thermally stable peroxyxynitrate is possible which might potentially result in the long range transport of NO<sub>x</sub>. However, although peroxyxynitrates of structure ROC(O)OONO<sub>2</sub> are thermally stable under atmospheric conditions<sup>33</sup> the CH<sub>3</sub>C(O)O entity in the peroxyxynitrate formed from acetoxyacetaldehyde, *i.e.* CH<sub>3</sub>C(O)OCH<sub>2</sub>C(O)OONO<sub>2</sub>, might render this particular susceptible to hydrolysis and thus rapid removal from the atmosphere.

Since the anhydrides produced in the atmospheric degradation of VA and AA are not very reactive toward either OH or Cl,<sup>38</sup> processes such as washout or heterogeneous hydrolysis on aerosols to form formic and acetic acids are probably the major atmospheric loss processes for these compounds.

Under low NO<sub>x</sub> conditions only the reaction of OH with VA will lead to the types of bond cleavage products listed above. The reaction of Cl with VA and the reactions of OH and Cl with AA will produce hydroxy acyl or chloro acyl compounds retaining the parent compound carbon skeleton. These compounds will not be very reactive toward OH and their atmospheric degradation, wither in the gas, aqueous or heterogeneous phase will probably result in acid formation, however, this may not necessarily occur close to the emission source.

It is probably safe to say that the both the OH-radical and Cl-atom mediated atmospheric degradation of VA and AA will result primarily in acid formation under both low and high NO<sub>x</sub> conditions but probably on different time scales.

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