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1   **Tropospheric chemical degradation of vinyl and allyl acetate initiated by**

2   **Cl atoms under high and low NO$_x$ conditions**

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22
23   **Abstract**
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25
26   The products of the reactions of Cl atoms with vinyl acetate (VA) and allyl acetate (AA) have been

27   investigated in a 1080 L chamber using *in situ* FTIR. The experiments were performed at 296 K and

28   atmospheric pressure of synthetic air in the presence and in the absence of NO$_x$. For the reaction of

29   Cl with VA in the presence of NO$_x$ formic acetic anhydride, acetic acid and formyl chloride are the

30   major reaction products. In the absence of NO$_x$, the yields of these products are significantly

31   reduced and formation of the carbon-chain-retaining compound $CH_3C(O)OC(O)CH_2Cl$ is observed.

32   For the reaction of Cl with AA in the presence of NO$_x$ acetoxyacetaldehyde and formaldehyde were

33   observed as the main products. In contrast, without NO$_x$, the observations support that the major

34   reaction pathway is formation of the carbon-chain-retaining compound $CH_3C(O)OCH_2C(O)CH_2Cl$.

35   The reaction mechanisms leading to the products are discussed. The formation of the high yields of

36   formyl chloride and formaldehyde in the reactions of Cl with VA and AA, respectively, are at odds

37   with currently accepted mechanistic pathways.
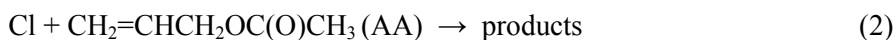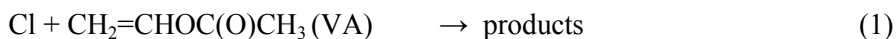
Introduction

40   In addition to emissions from natural sources (vegetation and biomass combustion) industrial

41   activities have resulted in the wide-spread release of acetates to the atmosphere.[1] Emissions from

42   automobiles represent another source of these compounds; a number of acetates, including vinyl

43   acetate (VA: $CH_3C(O)OCH=CH_2$) and allyl acetate (AA: $CH_3C(O)OCH_2CH=CH_2$), have been

44   detected as products in the combustion of rape methyl esters used as fuel alternatives or additive.[2]

45   The gas-phase removal processes of these esters from the atmosphere, and volatile organic

46   compounds (VOCs) in general, is mainly through their reactions with OH, NO_3, and O_3 with

47   removal by Cl being thought to play, under most circumstances, a very minor role since the global

48   Cl atom concentration is low ($<10^3$ radicals cm^{-3}).[3-5] The general conception has been that any

49   significant removal of VOCs through reaction with Cl atom is constrained to (i) the marine

50   boundary layer and coastal regions,[6-7] and (ii) industrial areas where chlorine can be emitted directly

51   from incineration and power generation.[8,9] However, a series of recent observations of nitryl

52   chloride ($ClNO_2$) in marine and mid-continental air[10-11] and in urban power plants plumes[12] have

53   highlighted the potential importance of $ClNO_2$ as a hither to unconsidered source of Cl and

54   indicated that the role of Cl in initiating the oxidation of VOCs may be more widespread and

55   significant than previously thought. Nitryl chloride is formed during the night via the heterogeneous

56   reaction of N_2O_5 with particle Cl^- and photolyzes readily in the early morning to produce Cl and an

57   NO_2 molecule.[13] A field and modelling study of Cl_2 and $ClNO_2$ in the coastal marine boundary layer

58   has recently been reported for the Los Angeles region.[14] The results indicated that over the course of

59   an entire model day $ClNO_2$ accounted for 45% of the integrated Cl-atom production compared to

60   only 10% for Cl_2 with the remaining 45% being attributed to the reaction of OH with HCl. The

61   study also showed that Cl-atom mediated chemistry could contribute quite substantially to the

62   photooxidation of VOCs in this region particularly in the early morning.

63   In order, to evaluate the contribution of VA and AA to the oxidative capacity of the atmosphere and

64   potential environmental and health effects detailed kinetic and mechanistic information on their

65   tropospheric gas-phase degradation pathways are required. There have been several kinetic studies

66   of the reactions of VA and AA with OH,[15-17] NO$_3$,[17] O$_3$[17] and Cl.[18] In addition, product studies on

67   the OH-radical initiated oxidation of these unsaturated esters have also been reported. Picquet-

68   Varrault et al. have reported product studies on the reactions of OH radicals with both VA[17] and

69   AA[19] performed at atmospheric pressure and room temperature in the presence of NO$_x$ using FTIR

70   spectrometry for the analyses. Picquet-Varrault et al.[17] reported formaldehyde, formic acetic

71   anhydride and acetic acid as the main products formed in the reaction of OH with VA. For the

72   reaction of OH with AA acetoxyacetaldehyde and HCHO were the main products observed.[19]

73   We have recently reported room temperature product investigations on the gas-phase reactions of

74   OH radicals with VA and AA in the presence and absence of NO$_x$.[20] Our results in the presence of

75   NO$_x$ agreed well with those reported by Picquet-Varrault et al.[17-19] for the two compounds.

76   However, our studies showed that in the absence of NO$_x$ there are significant changes in the relative

77   importance of the possible product channels for the reaction of the 1,2-hydroxyalkoxy radicals

78   formed after addition of OH to the double bond in the compounds. In the case of VA, an α-ester

79   rearrangement to produce $CH_3C(O)OH$ and $CH_2(OH)CO^{\bullet}$ radicals rather than decomposition to

80   form formic acetic anhydride dominated. In the case of AA reaction of the 1,2-hydroxyalkoxy

81   radical with O$_2$ to form the carbon chain-retaining product 3-hydroxy-2-oxo-propyl ester

82   ($CH_3C(O)OCH_2C(O)CH_2OH$) dominated in the absence of NO$_x$ contrasting very sharply with the

83   decomposition channel of the 1,2-hydroxyalkoxy radicals to form acetoxyacetaldehyde and HCHO,

84   which dominated when the reaction was studied in the presence of NO$_x$.

85 In a continuation of our investigations on the photooxidation mechanisms of unsaturated VOCs for

86 different NO_x scenarios, we report here product studies on the Cl-atom initiated photooxidation of

87 VA and AA in the presence and absence of NO_x:

88

89 $$Cl + CH_2=CHOC(O)CH_3\,(VA) \qquad \rightarrow\ products \qquad\qquad (1)$$

90 $$Cl + CH_2=CHCH_2OC(O)CH_3\,(AA)\ \rightarrow\ products \qquad\qquad (2)$$

91 A computational study on the mechanism and kinetics of the Cl-initiated oxidation of VA in the

92 presence of NO_x was reported recently.[21] The study found that Cl addition to the double bond is the

93 dominate pathway followed, in the presence of O_2 and NO, by decomposition to give the major

94 products observed in our work.

95 To the best of our knowledge this is the first reported experimental product investigation of the Cl-

96 atom initiated photooxidation for both VA and AA performed in the presence and in the absence of

97 NO_x.

98

99 **Experimental Section**

100

101 All the experiments were performed in a 1080 L quartz-glass reaction chamber at (298 ± 2) K and a

102 total pressure of (760 ± 10) Torr of synthetic air (760 Torr = 101.325 kPa). A detailed description of

103 the reactor can be found elsewhere[22] and only a brief description is given here. The photolysis

104 system consists of 32 superactinic fluorescent lamps (Philips TL05 40W: 320 – 480 nm, $\lambda_{max} = 360$

105 nm), which are spaced evenly around the reaction vessel. The chamber is equipped with a White

106 type multiple-reflection mirror system with a base length of (5.91 ± 0.01) m for sensitive *in situ*

107 long path infrared absorption monitoring of reactants and products in the spectral range 4000 – 700

108 cm^{-1}. The White system was operated at 82 traverses, giving a total optical path length of $(484.7 \pm$

109 0.8) m. Infrared spectra were recorded with a spectral resolution of 1 cm^{-1} using a Nicolet Nexus

110   FT-IR spectrometer equipped with a liquid nitrogen cooled mercury-cadmium-telluride (MCT)

111   detector.

112   Chlorine atoms were generated by the photolysis of Cl_2 using the fluorescent lamps:

113                          $Cl_2 + h\nu$ $\rightarrow$ 2 Cl   (3)
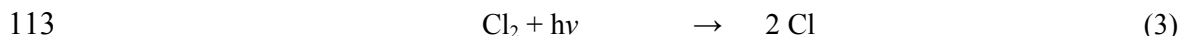
114   Experiments were performed on mixtures of Cl_2/acetate/air or Cl_2/acetate/NO/air which were

115   irradiated for periods up to 5 minutes during the course of which infrared spectra were recorded at 1

116   cm^{-1} resolution with the FTIR spectrometer. Tests showed that photolytic removal of the acetates in

117   the absence of Cl_2 and NO was negligible. The systems, in particular the AA system, are very

118   reactive and typically 20 interferograms were co-added per spectrum over a period of

119   approximately 5 min for the experiments with VA and 10 interferograms for the experiments with

120   AA. The concentrations of the reactants used in the experiments and the infrared frequencies used

121   for monitoring are given in the Supporting Information (SI).

122   The quantification of reactants and products was performed by comparison with calibrated

123   reference spectra contained in the IR spectral data bases of the laboratories in Wuppertal and

124   Laboratoire Interuniversitaire des Systemes Atmosphériques (LISA), Paris, France.[23]

125
126   **Results**

127   **Cl + Vinyl acetate**

128   <u>***NO_x-containing system***</u>*:* A typical product spectrum obtained after irradiation of a VA/Cl_2/air/NO

129   mixture and subtraction of residual absorptions due to VA is shown in Figure 1, panel A. Infrared

130   spectra of formic acetic anhydride, formyl chloride, acetic acid, and carbon monoxide are shown in

131   Figure 1, panels B, C, D and E, respectively. After subtraction of absorptions from these identified

132   products absorptions remain at 786, 853, 1193, 1322, 1698, 1801 and 3588 cm^{-1} as shown in Figure

133   1, panel F. The residual absorptions are due mainly to nitrosyl chloride (ClNO) and nitryl chloride

134   ($ClNO_2$) formed from the reactions of Cl atoms with NO and NO_2, respectively, and also some

135   nitric acid (HNO_3) formed through reaction of OH with NO_2 and heterogeneous reactions of NO_x at

136   the reactor wall. The reactions of NO with the HO_2 radicals formed in the system will produce OH

137   radicals, however, since the rate coefficients for Cl with VA is nearly an order of magnitude higher

138   than the corresponding OH reaction and OH is scavenged by NO_2, interference by OH chemistry

139   will be minimal. This also applies to the AA reaction system in the presence of NOx.

140   Concentration-time profiles of VA and the identified products, formic acetic anhydride, formyl

141   chloride, acetic acid and carbon monoxide are shown in Figure S1 of Supplementary Information

142   (SI). Plots of the concentrations of the identified products as a function of reacted VA are shown in

143   Figure S2. As can be seen in Figure S1 the increase in the product concentrations scale linearly

144   with the loss of VA supporting that the products are all primary and that secondary loss or

145   formation of these products is insignificant. The molar yields of the products observed in the

146   reaction of Cl with VA in the presence of NO_x, obtained from the slopes of the plots in Figure S2,

147   are listed in Table 1.

148

149   ___*NO$_x$-free system*___: Figure S3, panel A in the SI, shows the IR spectrum obtained after UV irradiation

150   of a VA/Cl_2/air mixture and subtraction of residual absorptions due to VA. Figure S3, panels B, C,

151   D, and E show reference spectra of formic acetic anhydride, formyl chloride, acetic acid and carbon

152   monoxide, respectively, all of which have been identified as products. Figure S3, panel F shows the

153   residual spectrum that is obtained after subtraction of absorptions from the identified products from

154   the spectrum in panel A; unidentified absorptions remain at approximately 1017, 1059, 1111, 1205,

155   1372 and 1808 cm^{-1}.

156   Many of the absorption features in the residual product spectrum correlate very well with those of

157   acetic acid anhydride and chloroacetone indicating that the compound (or compounds) giving rise to

158   the IR features contains structural elements common to both acetic acid anhydride and

159   chloroacetone. Since we are certain that all other possible reaction products from the reaction of Cl

160   with VA have been accounted for we are confident that the unidentified absorptions are mainly due

161   to the formation of the VA carbon-skeleton retaining compound chloro-acetic acid anhydride

162   ($CH_3C(O)OC(O)CH_2Cl$) although contributions from $CH_3C(O)OC(OH)CH_2Cl$ can not be excluded.

163   Further justification for the formation of $CH_3C(O)OC(O)CH_2Cl$ from the 1,2-chloroalkoxy radicals

164   formed in the Cl + vinyl acetate reaction are given in the discussion on the formation of

165    $CH_3C(O)OCH_2C(O)CH_2Cl$ in the reaction of Cl with allyl acetate.

166   Concentration-time profiles of VA and the four identified products are shown in the SI in Figure S4.

167   Plots of the concentrations of the products as a function of reacted VA for the NO_x-free reaction

168   system are shown in Figure 2. The plots are linear with near zero intercepts supporting that the

169   products are all primary. The molar yields of the products observed in the reaction of Cl with VA in

170   the absence of NO_x, obtained from the slopes of the plots in Figure 2, are listed in Table 1.

171

172   **Cl + Allyl acetate**

173   _NO$_x$-containing system:_ Panel A of Figure S5 in the SI shows a typical product spectrum acquired

174   after irradiation of a $AA/Cl_2/air/NO$ mixture and subtraction of residual absorptions due to AA.

175   Panels B, C, D, E and F show the reference spectrum of formic acetic anhydride, formyl chloride,

176   acetic acid, formaldehyde and acetoxyacetaldehyde ($CH_3C(O)OCH_2C(O)H$), respectively. These

177   compounds have been identified as products in the reaction system along with CO, the absorptions

178   of which can be seen around 2200 cm^{-1} in Figure S5, panel A. Panel G shows the residual spectrum

179   obtained after the subtraction of absorptions due the identified products. In the residual spectra

180   many absorption bands remain in the fingerprint region and in the region 1671 – 1808 cm^{-1}. As in

181   the VA system with NO_x some of these absorptions can be assigned unequivocally to nitrosyl

182   chloride, nitryl chloride and nitric acid. In addition, to these compounds, as will be argued in the

183   Discussion, bands at 1744, 1300, 1047 and 795 cm^{-1} are assigned to formation of acetoxyacetyl

184   peroxynitrate ($CH_3C(O)OCH_2C(O)OONO_2$).

185   Figure S6 shows the concentration-time profiles of AA and the identified products formed in the

186   NO_x-containing system. The profile of AA shows that it is being consumed very rapidly in the

187   system. The initial concentration-time profiles of acetoxyacetaldehyde and HCHO are similar and

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188   indicate that they are both primary products. However, secondary removal of acetoxyacetaldehyde

189   and especially HCHO in secondary reactions with Cl is clearly evident.

190   Although the concentration-time profiles of acetic acid, formic acetic anhydride and CO look as

191   though they may be primary products, plots of their concentrations against the amount of AA

192   consumed have non-zero intercepts and upward curvature which increases with increasing reaction

193   time (see Figure S7 in the SI). This behavior is indicative of formation of these compounds in

194   secondary reactions. The formation of acetic acid and formic acetic anhydride in the system is

195   attributed to fast secondary reactions of acetoxyacetaldehyde with Cl (see Discussion). Formation

196   of formyl chloride was also observed in the system; however, it was only observed in small

197   quantities toward the end of the reaction and is obviously being formed in secondary reactions.

198   The initial slopes of the plots of the concentrations of acetoxyacetaldehyde and HCHO against

199   reacted AA indicate high yields for both compounds. Taking the first few points of a plot of the

200   concentration of acetoxyacetaldehyde as a function of reacted AA gives a yield of

201   acetoxyacetaldehyde of close to unity, however, if all the points are taken a yield of around 66% is

202   obtained caused by curvature in the plot from fast secondary reaction of acetoxyacetaldehyde with

203   Cl. Correction of yield for formaldehyde for secondary consumption with Cl using the method

204   outlined in Tuazon et al.[24] and a rate coefficient of 7.32×10^{-11} cm^3 $molecule^{-1}$ s^{-1} for the reaction of

205   Cl with HCHO[25] gives a yield of >90 % for HCHO. The rate coefficient for the reaction of Cl with

206   acetoxyacetaldehyde is not known. Using the rate coefficient for Cl with HCHO for the correction

207   gave a yield of around 120%. Since the rate coefficient for Cl with acetoxyacetaldehyde is not

208   likely to be much less than that for Cl with HCHO this would support a yield much higher than 66%

209   yield for acetoxyacetaldehyde.

210

211   _**NOₓ-free system**_: The irradiation of a AA/Cl₂/air mixture give rise to the product spectrum shown

212   in Figure S8, panel A. Formation of minor amounts of acetoxyacetaldehyde, formic acetic

213   anhydride, acetic acid and formaldehyde were observed but the molar yields for each of these

214   products was < 5% (Table 1). Reference spectra of chloroacetone and methyl acetate are shown in

215   Figure S8, panels B and C, respectively. It can be seen that the product spectrum in Figure S8, panel

216   A, contains absorption features that match those in both the spectrum of methyl acetate and that of

217   chloroacetone. In fact, when these two spectra are mathematically added the resulting spectrum

218   almost completely matches all of the features in the residual product spectrum supporting that the

219   compound must contain the $CH_3C(O)O-$ and $-COCH_2Cl$ entities. Since addition of Cl will be

220   predominately at the terminal carbon of the double bond and the yields of carbon cleavage products

221   are minimal we are quite confident that the absorptions in the IR spectrum in Figure S8, panel A,

222   are predominantly due to the formation of acetic acid 3-chloro-2-oxo-propyl ester

223    $(CH_3C(O)OCH_2C(O)CH_2Cl)$. Formation of $CH_3C(O)OCH_2CH(Cl)C(O)H$ and other hydroperoxy

224   and hydroxyl compounds from peroxy-peroxy reactions in the system are obviously also possible,

225   however, based on the observed infrared product spectra, we estimate that the yields of these

226   compounds must be very low. For example, $CH_3C(O)OCH_2CH(Cl)C(O)H$ would not give rise to

227   the strong absorptions observed at around 1245 and 1050 cm^{-1}. Formation of the compound would

228   also not be in line with the high observed yield of acetoxyacetaldehyde in the NO_x-containing

229   system. It is well established that a major channel in the reactions of the 1,2-chloroalkoxy radicals

230   formed in the addition of Cl to alkenes is reaction of the 1,2-chloroalkoxy radicals with O_2 to form a

231   1,2-chloro carbonyl compound[26], for example, Butt et al. (2009)[27] have observed carbon-skeleton

232   retaining compound $C_4F_9CH_2CH_2OC(O)C(O)CH_2Cl$ as a major product from the addition of Cl to

233   4:2 fluorotelomer acrylate $(C_4F_9CH_2CH_2OC(O)CH=CH_2)$ both in the presence and absence of NO_x.

234   Further support comes from recent work on long chain C_x to C_9 terminal alkenes by Walavalkar et

235   al.[28] which showed that addition of Cl to the inner carbon of the double bond is minimal and that 1-

236   chloro-2-ketones are the main products in the absence of NO_x. The above points serve to strengthen

237   the arguments offered for the identification of acetic acid 3-chloro-2-oxo-propyl ester as the main

238   product in the reaction of Cl with ally acetate in the absence of NO.

239   The near quantitative formation of acetic acid 3-chloro-2-oxo-propyl ester in the reaction of Cl with

240   AA in the absence of NOx allows an approximate IR calibration of the compound. Using a band at

241   3415 cm^{-1} which is unique to the compound allows a yield of $\leq$ 5 % to be placed on the formation of

242   the ester in the reaction of Cl with AA in the presence of NO_x.

243

244   **Discussion**

245

246   **Cl + Vinyl acetate**

247   *Reaction with NO_x*: As can be deduced from Table 1 the carbon balance for the reaction of Cl with

248   VA in the presence of NO_x is, within the error limits, approximately 100 %. The reaction will

249   proceed via addition of Cl to the double bond followed by consecutive addition of O_2 and reaction

250   with NO form $CH_3C(O)OCH(O^{\cdot})CH_2Cl$ alkoxy radicals (Figure 3, channel A). Three channels are

251   traditionally thought be operative for the radicals, decomposition, an α-ester rearrangement and

252   reaction with O_2, Figure 3, channels B, C and D, respectively. The later channel is not observed

253   with NO. Decomposition to form formic acetic anhydride with a yield of (69 $\pm$ 8) % is observed.

254   The expected co-product is the $Cl\text{-}CH_2^{\cdot}$ radical which would be expected to add O_2 giving peroxy

255   radicals which react further with NO to form $Cl\text{-}CH_2O^{\cdot}$ alkoxy radicals. Further reaction of these

256   radicals with O_2 are a potential pathway to the HC(O)Cl detected in the system.

257   However, Bilde et al.[29] have studied the reaction of $Cl\text{-}CH_2^{\cdot}$ radicals in N_2 with different partial

258   pressures of O_2 in the presence and absence of NO_x. They produced the radicals via reaction of Cl

259   with CH_3Cl. They did not measure the decay of CH_3Cl since this was too small and determined the

260   product yields from the sum of the three identified carbon-containing products HCOCl, HCHO and

261   CO which they assumed was equal the amount of consumed CH_3Cl. They found that in the absence

262   of NO_x the final product was HC(O)H in nearly 100 % yield and that with NO_x in 700 Torr of air

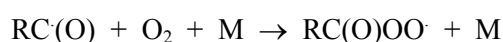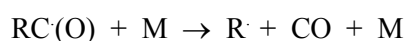263   HC(O)Cl, HC(O)H and CO were products with yields of (56 $\pm$ 10), (32 $\pm$ 6) and (12 $\pm$ 5)%,

264   respectively. The result of Bilde et al. with NO_x contrasts sharply with the large yield of HC(O)Cl

265   and no HC(O)H observed in the reaction of Cl with VA in the presence of NO_x presented here.

266   Bilde et al.[29] attributed the differences in the yields of HC(O)Cl with and without NO_x to the

267   formation of excited Cl-CH$_2$O$^{\cdot}$* alkoxy radicals in the exothermic reaction of Cl-CH$_2$OO$^{\cdot}$ peroxy

268   radicals with NO_x whereas in the NO_x-free system only thermalized Cl-CH$_2$O$^{\cdot}$ radicals are formed

269   through nearly thermo neutral peroxy-peroxy reactions.

270   At present it is difficult to explain why we observe mainly formation of HC(O)Cl from the reactions

271   of the Cl-CH$_2$$^{\cdot}$ radical formed in the reaction of Cl with VA in the presence of NO_x in contrast to the

272   findings of Bilde et al.[29] The situation is made even more curious by the fact that in the

273   Cl/AA/NO/air system we observe HC(O)H as the co-product of acetoxyacetaldehyde and not

274   HC(O)Cl. One obvious difference is the source of the Cl-CH$_2$$^{\cdot}$ radicals in the studies. Our

275   observations imply that the decomposition channel is not as straightforward as depicted in Figure 3,

276   i.e. the mechanism is much more complex and may not involve formation of Cl-CH$_2$$^{\cdot}$ radicals.

277   The only structural difference between vinyl acetate and allyl acetate is the –CH$_2$- group in ally

278   acetate between the oxygen atom and the double bond. This difference is structure is apparently

279   critical in determining the reaction products resulting from the terminal –CH$_2$Cl group after

280   consecutive addition of Cl and O$_2$ to form 1,2-chloroperoxy radicals. The carbonyl and C-Cl entities

281   in the intermediate 1,2-chloroperoxy radical reaction intermediates are strongly electron

282   withdrawing. It is possible that there are bonding interactions between the peroxy radicals and the

283   carbonyl and C-Cl entities in the reaction intermediates which complicate the reactions of NO and

284   propably also HO$_2$/RO$_2$ radicals with the 1,2-chloroperoxy radical intermediates and thus the

285   reaction pathways and products. The 1,2-chloroperoxy radical formed in the reaction of Cl with

286   allyl acetate could form a weakly bound six-membered ring with the carbonyl group which would

287   be more favorable than a five-membered ring which could be formed in the reaction of Cl with

288   vinyl acetate. Interaction of the peroxy group with C-Cl and NO could potentially result in the

289   product of chemically activated CH$_2$ClO radicals especially in the case of vinyl acetate where

290   interaction of the peroxy group with the carbonyl group is probably not as important as for allyl

291   acetate. This is presently purely speculation and obviously more detailed laboratory studies as a

292   function of temperature, pressure and O_2 and in particular computational studies are needed to shed

293   light on the mechanistic differences observed in the reactions of Cl with vinyl acetate and allyl

294   acetate in the presence and absence of NO.

295   The other important channel in the reaction of Cl with VA involves an ester rearrangement[30] to

296   form $CH_3C(O)OH$ with a yield of (27 ± 5) % and the halogenated acyl radical $Cl\text{-}CH_2C^.(O)$. There

297   are two known fates of acyl radicals either thermal decomposition or addition of O_2 to form

298   acylperoxy radicals:[31-34]

$$RC^.(O) + M \rightarrow R^. + CO + M$$

$$RC^.(O) + O_2 + M \rightarrow RC(O)OO^. + M$$

301   For acyl radicals addition of O_2 at atmospheric pressure and room temperature is known to

302   dominate,[33,34] however, there is a known monotonic trend towards decomposition, at 298 K and

303   atmospheric pressure of air, with increase in the number of Cl in the $CCl_xF_{3-x}C^.(O)$ radical.[28,29]

304   Although a theoretical study on the atmospheric fate of carbonyl radicals predicts that the main fate

305   of the $Cl\text{-}CH_2C^.(O)$ radical is addition of O_2 and not decomposition the experimental observations

306   in this study of primary CO formation suggests rapid decomposition of the the $Cl\text{-}CH_2C^.(O)$ radical

307   into CO and a $Cl\text{-}CH_2^.$ radical rather than addition of O_2 (Figure 3, channel C).

308   If addition of O_2 to $Cl\text{-}CH_2C^.(O)$ was an important channel the peroxy radicals formed would, due

309   to the high NO_2 levels, add NO_2 to a significant extent to form the thermally stable PAN type

310   compound $ClCH_2C(O)OONO_2$. No evidence could be found in the product spectra for the formation

311   of a PAN type compound.

312   During this writing a computational study on the mechanism and kinetics of the Cl-initiated

313   oxidation of VA appeared.[21] The study found that H-atom abstraction pathways were negligible and

314   that Cl addition dominated followed, in the presence of O_2 and NO, by decomposition to give

315     $CH_3C(O)OC(O)H$, $CH_3C(O)OH$ and $HC(O)Cl$ as major products as observed in this work. The

316   product channels observed for the reaction of Cl with VA in the presence of NO_x are similar to

317   those observed in the analogous OH reaction,[20] however, with a higher preference for the channel

318   forming $CH_3C(O)OC(O)H$ in the OH reaction.

319   *Reaction without NO_x*: In Figure 3 the peroxy radicals formed after reaction of Cl with VA are

320   shown to form wholly alkoxy radicals via reaction with HO_2 or other peroxy radicals. Other

321   pathways are known to form a hydroperoxy or alcohol, however, the yields of detected products and

322   residual IR product spectra suggest that these are relatively minor channels for both the VA and AA

323   systems. In the absence of NO_x, the two decomposition channels producing $CH_3C(O)OC(O)H$ and

324   HCOCl (Figure 3, channel B) and the ester rearrangement producing $CH_3C(O)OH$, CO and HCOCl

325   (Figure 3, channel C) are observed for the $CH_3C(O)OCH(O^\cdot)CH_2Cl$ radicals formed in the reaction

326   of Cl with VA. However, compared to the system with NO_x the relative contributions of these

327   channels to the overall reaction are much reduced with the channels B and C accounting for only

328   (25 ± 5) and (12 ± 3) % of the overall reaction, respectively. The combined yield of $HC(O)Cl$ from

329   these two channel was (48 ± 8) %.

330   The results clearly show that in the absence of NO_x, only approximately 50% of the reaction is

331   proceeding by the decomposition and rearrangement/decomposition channels of the chloroalkoxy

332   radicals (Figure 3, channels B and C). As indicated in the Results section the experimental

333   observations support the occurrence of a molecular channel with the formation of chloro-acetic acid

334   anhydride ($CH_3C(O)OC(O)CH_2Cl$) through the reaction of the $CH_3C(O)OCH(O\bullet)CH_2Cl$ with O_2

335   (Figure 3, channel D). Based on the carbon balance the yield of chloro-acetic acid anhydride could

336   be potentially as high as 50%. Unfortunately no calibrated reference spectrum is available to verify

337   this.

338   This result for the reaction of Cl with VA in the absence of NO_x contrasts quite markedly with that

339   for the analogous OH reaction under the same conditions. For the reaction of OH with VA in the

340   absence of NO_x a molecular channel is not observed. The absence of NO_x just results in a stark

341   switch in the preference of the two decomposition channels, i.e. the ester rearrangement channel

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342 dominates in the absence of NO_x compared to a dominance of the anhydride forming channel in the

343 presence of NO_x.[20] The substantially lower yields of primary decomposition products for the

344 reaction of Cl with VA in the absence of NO_x suggests that chemical activation is important in the

345 atmospheric chemistry of $CH_3C(O)OCH(O^{\cdot})CH_2Cl$ alkoxy radicals.

346 **Cl + Allyl acetate**

347 *Reaction with NO_x:* In this reaction system Cl adds mainly to the terminal carbon of the double

348 bond in AA followed by the addition of O_2 to give peroxy radicals which subsequently react with

349 NO to form 1,2-chloroalkoxy radicals as shown in Figure 4, channel A. Possible reaction channels

350 include decomposition to form acetoxyacetaldehyde and CH_2Cl radicals (channel B), decomposition

351 to form chloroacetaldehyde and $CH_3C(O)OCH_2$ radicals (channel C) or reaction with O_2 to form the

352 chain-retaining product $CH_3C(O)OCH_2C(O)CH_2Cl$ (Figure 4, channel D).

353 There was no indication for formation of chloroacetaldehyde in the product spectrum showing that

354 channel C is a negligible reaction pathway. As discussed below, from the study on the reaction of

355 Cl with AA in the absence of NO_x we are able to put a yield of ≤ 5 % on the formation of

356 $CH_3C(O)OCH_2C(O)CH_2Cl$ from the reaction of the 1,2-chloroalkoxy radicals with O_2 (channel D)

357 in the presence of NO_x.

358 In the product study with NO_x, acetoxyacetaldehyde, and formaldehyde have been identified as

359 major primary products. The results indicate that the major reaction channel after addition of is

360 cleavage of the C-C bond to form acetoxyacetaldehyde and potentially $CH_2Cl^{\cdot}$ radicals (Figure 4,

361 channel B).

362 As discussed in the Results section although a lower limit of 66% is given in Table for the yield of

363 acetoxyacetaldehyde the observations would suggest that after correction it would be close to unity.

364 In stark contrast to the reaction of Cl with VA in the presence of NO, HC(O)H is detected as the

365 main co-product originating from the decomposition channel and not HC(O)Cl. As in the

366 VA/Cl/NO/air system, based on the study of Bilde et al.,[29] this observation is again in strong

367 contrast to what would be expected from further reactions of the $ClCH_2^{\cdot}$ radical in the presence of
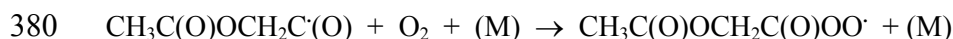
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368   NO. As discussed in the section on the reaction of Cl with NO the decomposition channel as shown

369   in Figure 4 for the reaction of Cl with AA would appear to be much more complex. Insertion of a –

370   CH_2- group between the acetoxy and double bond of VA and AA has resulted in the chlorinated

371   terminal carbon of the compounds producing HC(O)Cl in the case of VA and HC(O)H in the case

372   of AA. The classically accepted mechanism involving C-C cleavage to form $CH_2Cl^{.}$ radicals can not

373   explain the present product observations in the VA and AA reaction systems.

374   In addition to the fast secondary reaction of HCHO in the reaction system there is obviously also

375   considerable secondary reaction of acetoxyacetaldehyde with Cl. This reaction will proceed mainly

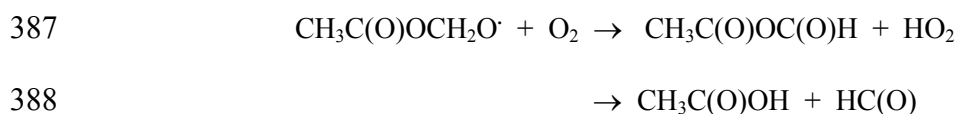376   through H-atom abstraction from the aldehydic hydrogen:

377    $CH_3C(O)OCH_2C(O)H + Cl \rightarrow CH_3C(O)OCH_2C^{.}(O) + HCl$

378   The resulting acyl radicals are expected, under the experimental conditions, to predominantly add

379   O_2 to form peroxy radicals rather than decompose:

380    $CH_3C(O)OCH_2C^{.}(O) + O_2 + (M) \rightarrow CH_3C(O)OCH_2C(O)OO^{.} + (M)$

381   In the reaction system the peroxy radicals can react with NO or add NO_2. Reaction with NO will

382   result mainly in the formation of $RC(O)O^{.}$ radicals which lose CO_2 and form $CH_3C(O)OCH_2^{.}$

383   radicals. These radicals undergo further consecutive reactions with O_2 and NO to give

384    $CH_3C(O)OCH_2O^{.}$ radicals.

385   There are two possible reaction pathways for the $CH_3C(O)OCH_2O^{.}$ radical either reaction with O_2 to

386   form formic acetic anhydride or an α-ester rearrangement to form acetic acid and HC(O) radicals.

387    $CH_3C(O)OCH_2O^{.} + O_2 \rightarrow CH_3C(O)OC(O)H + HO_2$

388    $\rightarrow CH_3C(O)OH + HC(O)$

389   Both acetic acid and formic acetic anhydride have been detected as products in the Cl + AA

390   reaction system in the presence of NO_x. We attribute the formation of both of these compounds to

391   secondary reactions of acetoxyacetaldehyde with Cl though the sequence of reactions outlined

392   above. The ratio of the yield of acetic acid to formic acetic anhydride is approximately 4:1 and

393   remains fairly constant throughout the reaction. Picquet-Varrault et al.[35] have obtained yields of 75

394   and 15 for the formation of acetic acid and acetoxyacetaldehyde in the reaction of OH with ethyl

395   acetate which also involves an α-ester rearrangement. The ratio of the two products is quite similar

396   to that obtained in this study for Cl with acetoxyacetaldehyde and we take this as an additional

397   endorsement that secondary reaction of Cl with acetoxyacetaldehyde is the source of acetic acid and

398   formic acetic anhydride in the Cl + AA reaction system. Picquet-Varrault et al.[19] in their study on

399   the reaction of OH with AA found acetoxyacetaldehyde as the main product and strongly suspected

400   that secondary reactions of this compound led to the formation of formic acetic anhydride and

401   acetic acid that they observed in their reaction system. This study supports that the reactions of OH

402   and Cl with acetoxyacetaldehyde are similar and result in formation of formic acetic anhydride and

403   acetic acid.

404   Reaction of the peroxy radicals formed in the reaction of Cl with acetoxyacetaldehyde with NO_2

405   will lead to the formation of a peroxynitrate.

406    $$CH_3C(O)OCH_2C(O)O_2 + NO_2 + (M) \rightarrow CH_3C(O)OCH_2C(O)O_2NO_2 + (M)$$
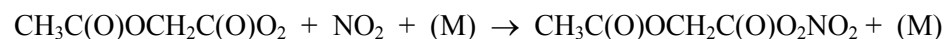
407   This type of peroxynitrate is expected to be reasonably stable at room temperature and atmospheric

408   pressure.[36,37] Indeed, bands are present in the product spectrum which can be assigned to a

409   peroxynitrate. Trace A in Figure 5 shows the spectrum that is obtained at the end of the irradiation

410   of a $AA/Cl_2/NO_x$ reaction mixture after subtraction of acetoxyacetaldehyde, acetic acid, formic

411   acetic anhydride and nitric acid. The * symbols highlight bands that are characteristic for the

412   formation of a peroxynitrate.[36] The band at ~1744 cm^{-1} can be assigned to an asymmetric stretching

413   band of NO_2 (asym. NO_2), that at ~1330 cm^{-1} to a symmetrical stretch of NO_2 (sym. NO_2) and that

414   at ~795 cm^{-1} to a NO_2 deformation. A band at ~1045 cm^{-1} is also observed. Bands in this region are

415   observed in the infrared spectra of many peroxynitrates, however, we have no vibrational group

416   assignment for this band.

417   Trace B, Figure 5 shows a difference spectrum obtained after subtraction of the first spectrum in

418   which the AA concentration was zero from the last spectrum in the experiment. This spectrum

419 shows the continuing secondary decay of the main product acetoxyacetaldehyde (# symbols) and

420 the formation of the bands that we assign to a peroxynitrate. The experimental evidence supports

421 that the peroxynitrate absorptions are arising predominantly from the formation of thermally stable

422 acetoxyacetyl peroxynitrate.

423

424 *Reaction without NO$_x$:* As discussed in the Results section, the experimental observations support

425 that the fate of the $CH_3C(O)OCH_2CH(O^{\cdot})CH_2Cl$ alkoxy radicals formed in the Cl + AA reaction in

426 the absence of NO$_x$ is essentially reaction with O$_2$ to form acetic acid 3-chloro-2-oxo-propyl ester

427 $(CH_3C(O)OCH_2C(O)CH_2Cl)$. The analogous OH reaction in the absence of NO$_x$ has been observed

428 to form mainly 3-hydroxy-2-oxo-propyl ester $(CH_3C(O)OCH_2C(O)CH_2OH)$[20] through reaction

429 $CH_3C(O)OCH_2CH(O^{\cdot})CH_2OH$ alkoxy radicals with O$_2$, however, a ~26 % contribution from the

430 decomposition channel to form acetoxyacetaldehyde and HCHO was also observed.

431

432 **Atmospheric Implications**

433
434 As discussed in several publications the main tropospheric chemical removal of unsaturated

435 compounds is reaction with OH radicals and in the case of VA and AA the tropospheric lifetimes

436 respect to degradation through reaction with OH radicals are approximately 3 and 5 h,

437 respectively,[15-20] indicating that these VOCs will be rapidly degraded in the gas phase and near to

438 their emissions sources. The tropospheric lifetimes of the degradation of VA and AA initiated by Cl

439 atoms are 9 and 4 days, respectively.[18] However, in marine and industrialised continental regions,

440 where high chlorine concentrations can occur especially at dawn, Cl- mediated degradation of the

441 compounds may be able to compete with the OH- initiated oxidation. Under high NO$_x$ conditions

442 both the OH and Cl initiated oxidation of both compounds will give rise to high yields of bond

443 cleavage products including HCHO, HCOCl, $CH_3C(O)OH$, formic acetic anhydride and

444 acetoxyacetaldehyde. Further breakdown of acetoxyacetaldehyde will produce more acetic acid and

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445   formic acetic anhydride whereby formation of a potentially thermally stable peroxynitrate is

446   possible which might potentially result in the long range transport of NO_x. However, although

447   peroxynitrates of structure $ROC(O)OONO_2$ are thermally stable under atmospheric conditions[33] the

448   $CH_3C(O)O$ entity in the peroxynitrate formed from acetoxyacetaldehyde, i.e.

449   $CH_3C(O)OCH_2C(O)OONO_2$, might render this particular susceptible to hydrolysis and thus rapid

450   removal from the atmosphere.

451   Since the anhydrides produced in the atmospheric degradation of VA and AA are not very reactive

452   toward either OH or Cl[38] and processes such as washout or heterogeneous hydrolysis on aerosols to

453   formic and acetic acids are probably the major atmospheric loss processes for these compounds.

454   Under low NO_x conditions only the reaction of OH with VA will lead to the types of bond cleavage

455   products listed above. The reaction of Cl with VA and the reactions of OH and Cl with AA will

456   produce hydroxy acyl or chloro acyl compounds retaining the parent compound carbon skeleton.

457   These compounds will not be very reactive toward OH and their atmospheric degradation, wither in

458   the gas, aqueous or heterogeneous phase will probably result in acid formation, however, this may

459   not necessarily occur close to the emission source.

460   It is probably safe to say that the both the OH and Cl mediated atmospheric degradation of VA and

461   AA will result primarily in acid formation under both low and high NO_x conditions but probably on

462   different time scales.

463
464   **Acknowledgments**

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471   **Supporting Information**

472   Extensive supporting information, mainly in the form of diagrams as indicated in the text, is

473   available free of charge via the Internet at http://pubs.rsc.org.

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476   **References**
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615 **Figure Captions**

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618 **Figure 1.** Panel A shows the product spectrum obtained from the irradiation of a VA/Cl$_2$/NO/air

619 reaction mixture. Panels B, C. D and E show reference spectra of formic acetic anhydride, formyl

620 chloride, acetic acid, and carbon monoxide, respectively. Panel F shows the residual product

621 spectrum obtained after the subtraction of the identified products.
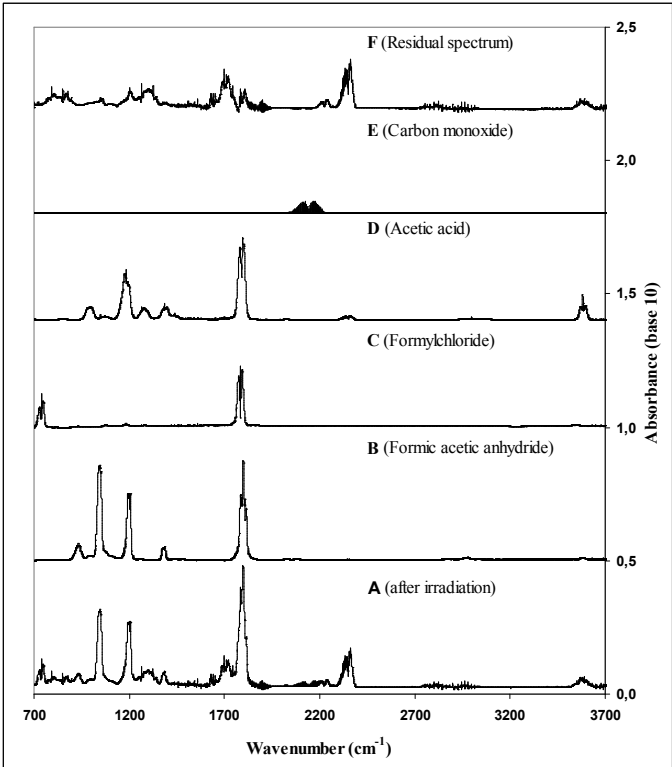
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623 **Figure 2:** Plot of the concentrations of the products formed in the reaction of Cl with VA in the

624 absence of NO as a function of the amount of reacted VA.

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627 **Figure 3.** Simplified mechanism for the Cl-atom initiated oxidation of VA (CH$_2$=CHOC(O)CH$_3$)

628 via addition of Cl to the terminal carbon of the double bond.

629

630 **Figure 4.** Simplified mechanism for the Cl-atom initiated oxidation of AA

631 (CH$_2$=CHCH$_2$OC(O)CH$_3$) via addition of Cl to the terminal carbon of the double bond.

632

633 **Figure 5:** Trace A shows the spectrum obtained at the end of the irradiation a AA/Cl$_2$/NO$_x$ reaction

634 mixture after subtraction of acetoxyacetaldehyde, acetic acid, formic acetic anhydride and nitric

635 acid. The * symbols in are attributed to the formation of acetoxyacetyl peroxynitrate. Trace B is the

636 difference spectrum obtained after subtraction of the first spectrum in which the AA was zero from

637 the last spectrum in the experiment. This spectrum demonstrates the secondary decay of the main

638 product acetoxyacetaldehyde (# symbols) and the formation of acetoxyacetyl peroxynitrate (*
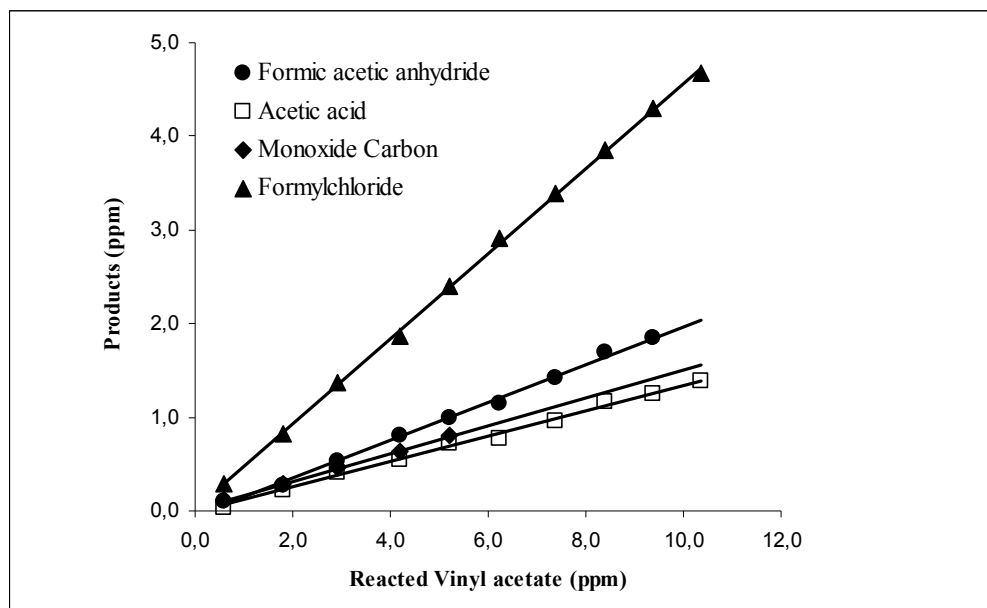
639 symbols).

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643   **Figure 1**

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667 **Figure 2**

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710 **Figure 3**

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758 **Figure 4**
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805 **Figure 5**

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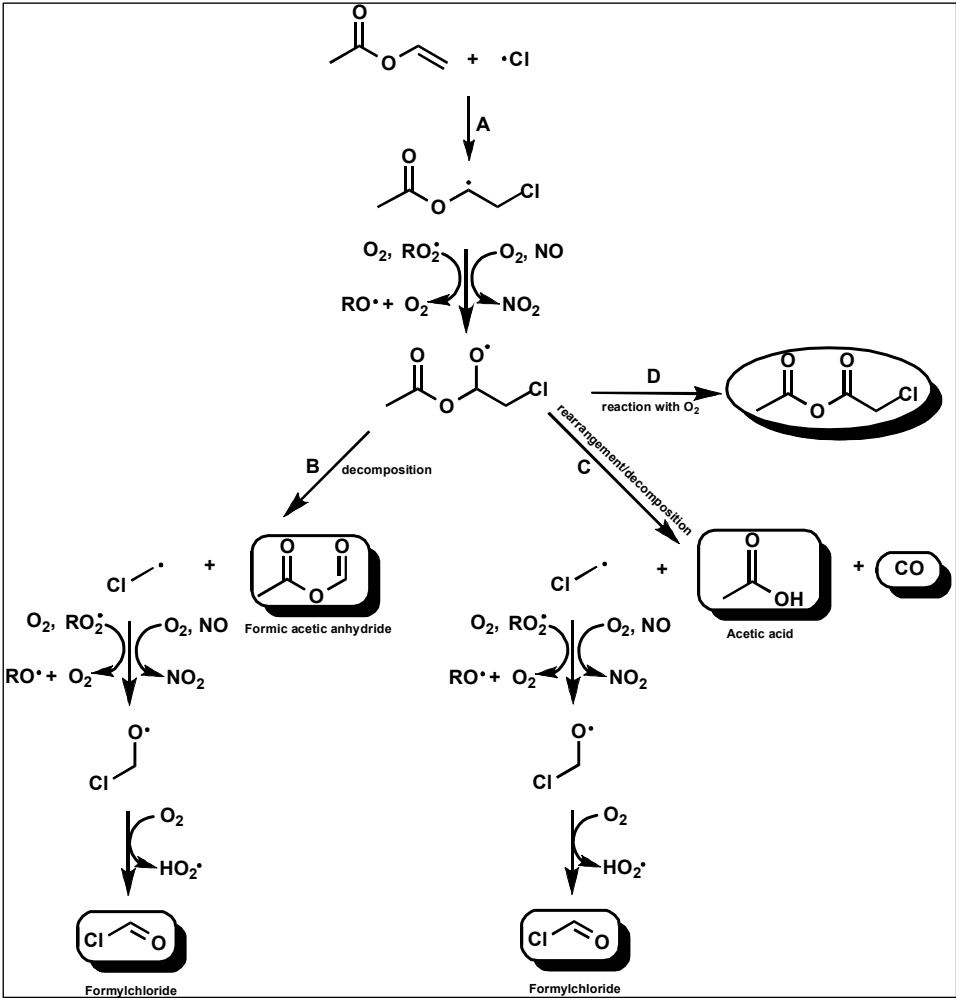816
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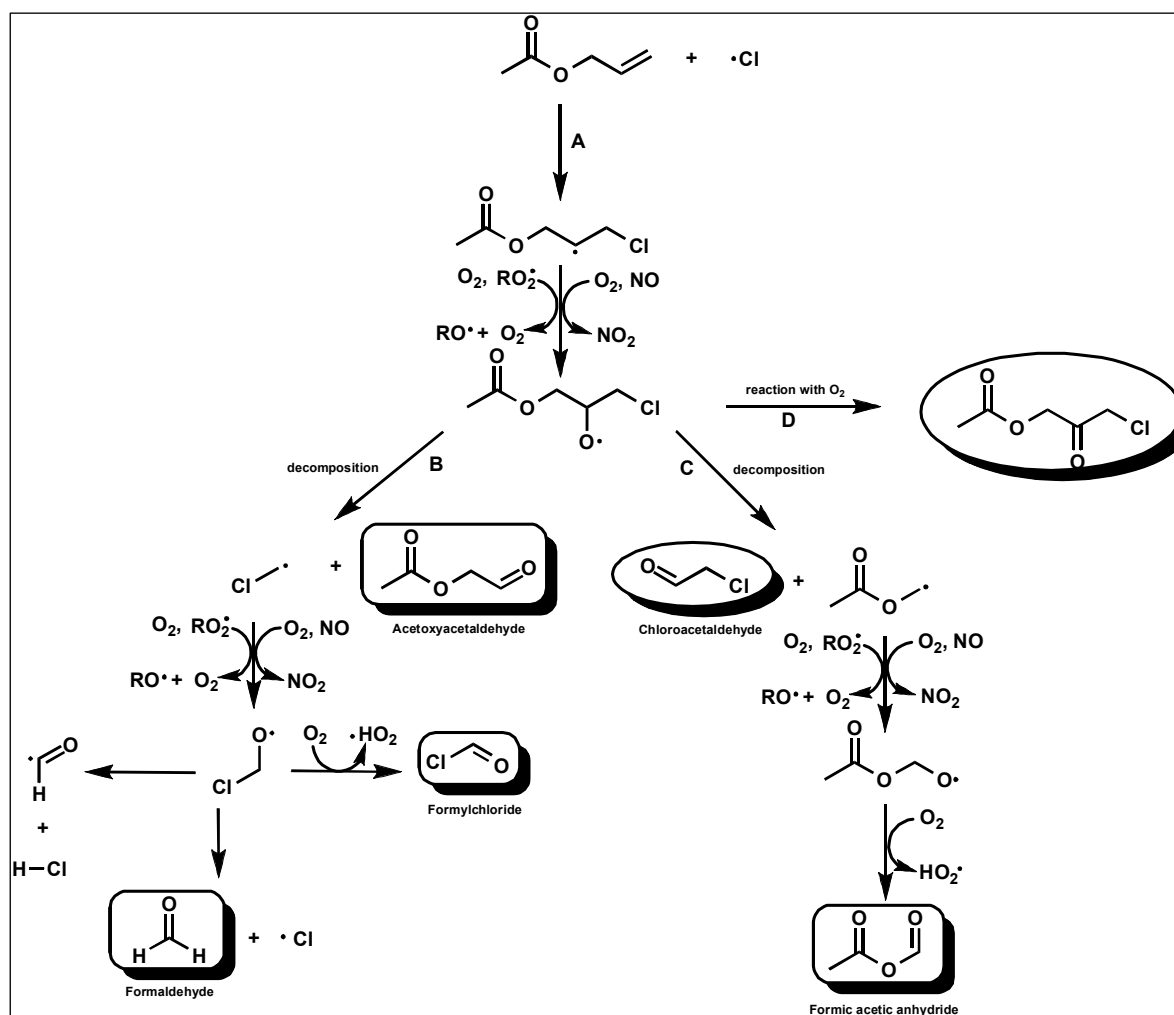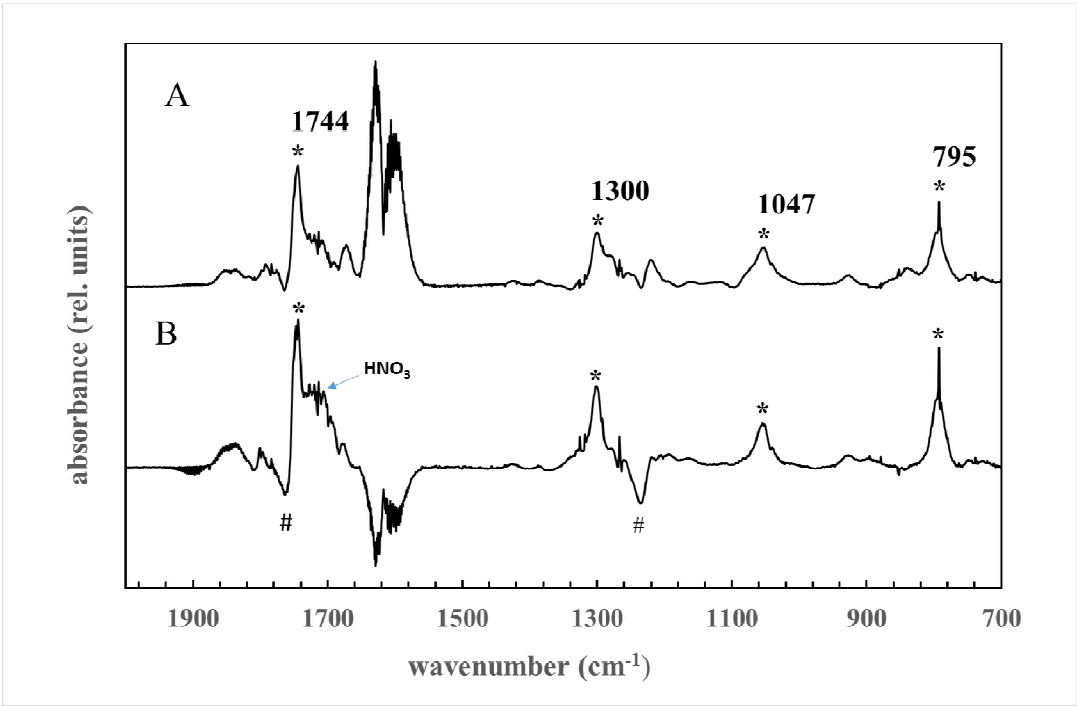821
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834   **Table 1:** Formation yields of the oxidation products identified from the Cl atom oxidation
835   of vinyl and allyl acetate studied in the presence and the absence of NO_x.
836   The quoted errors are the 2σ statistical errors from the linear regression analyses.

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Acetate	Product	Yield (%) (NO_x - containing)	Yield (%) (NO_x – free)
$CH_3C(O)OCH=CH_2$ **(vinyl acetate)**	$CH_3C(O)OC(O)H$ (Formic acetic anhydride)	69 ± 8	25 ± 5
	$CH_3C(O)OC(O)CH_2Cl$	-	~ 50[a]
	$CH_3C(O)OH$	27 ± 5	12 ± 3
	$HC(O)Cl$	94 ± 12	48 ± 8
	$HC(O)H$	≤ 5	-
	CO	30 ± 5	15 ± 4
$CH_3C(O)OCH_2CH=CH_2$ **(allyl acetate)**	$CH_3C(O)OCH_2C(O)H$ (Acetoxyacetaldehyde)	66 ± 8[a]	≤ 5
	$CH_3C(O)OCH_2C(O)CH_2Cl$	≤ 5	≥ 95[b]
	$CH_3C(O)OC(O)H$ (Formic acetic anhydride)	secondary	≤ 5
	$CH_3C(O)OH$	secondary	≤ 5
	$HC(O)Cl$	secondary	≤ 5
	$HC(O)H$	> 90	≤ 5
	CO	secondary	≤ 5

839   [a] Lower limit observations and attempted corrections for secondary consumption support much
840   higher yield (see text); [b] Estimate based on experimental observations.

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