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1 # Gas-phase reaction of two unsaturated ketones with Cl atom and O$_3$: kinetics and

2 # products

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7 **Abstract**:

8 The rate constants and products for the reactions of Cl atom and O$_3$ molecule with 3-methyl-3-buten

9 -2-one (MBO332) and 3-methyl-3-penten-2-one (MPO332) were determined in a 100 L Teflon

10 chamber at 293±1K and atmospheric pressure. For MBO332 and MPO332, the rate constants with Cl

11 atom measured were (2.38±0.26) ×10^{-10} and (3.00±0.34) ×10^{-10} cm^{3}molecule^{-1}s^{-1} using the relative

12 rate method. Using the absolute rate method, the rate constants with O$_3$ measured were (1.18±0.21)

13 ×10^{-17} and (4.07±0.45) ×10^{-17} cm^{3}molecule^{-1}s^{-1}. The products of these reactions were investigated by

14 the proton-transfer-reaction mass spectrum (PTR-MS). The results indicated that the major products

15 observed in the Cl atom reaction were formaldehyde together with chloroacetone for MBO332, and

16 acetaldehyde and CH$_3$C(O)C(O)Cl for MPO332. For O$_3$ reactions,

17 butanedione and formaldehyde were the main products of MBO332, while butanedione and

18 acetaldehyde were the main products of MPO332. Possible reaction mechanisms were proposed and

19 discussed and atmospheric implications of these reactions were also discussed.

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26 **Introduction**

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27   Owing to their significant global emission and reactivity towards atmospheric oxidants, volatile

28 organic compounds (VOCs) have great influence on atmospheric chemistry and radiative forcing[1-4].

29 In the atmosphere, unsaturated oxygenated VOCs have been identified as considerable components

30 of organic compounds such as alcohols, ethers, esters, aldehydes, and ketones [5]. They are released to

31 the atmosphere directly from biogenic and anthropogenic sources, and also formed from complex

32 secondary sources like degradation of hydrocarbons being in the atmosphere[6-8]. Once in the

33 troposphere, they will be subjected to undergo oxidation reactions by OH radical (mainly during the

34 day), NO_3 radical (at night), O_3 molecule and Cl atom (in certain environment)[9], and they have a

35 direct impact on atmospheric chemical processes via controlling ozone and secondary organic

36 aerosol formation [10, 11].

37   Unsaturated ketones are ubiquitous parts among the VOCs mentioned above in the troposphere,

38 and they are expected to have a number of different sources. For example, 3-methyl-3-buten-2-one

39 (MBO332) has been observed from plants, biomass burning, residential wood and fuel

40 combustion[12-15]. Emissions of 3-methyl-3-penten-2-one (MPO332) have been reported to be from

41 medicine plants in the Nepal and cut-induced agricultural grasslands[16, 17]. In addition, MBO332 and

42 MPO332 have been found to be intermediate products in synthesis and catalytic industry[18-20].

43 Therefore, it is necessary to acquire kinetics and mechanisms of gas-phase degradation of

44 unsaturated ketones for their environmental impact assessment.

45   Although oxidation of VOCs by OH radicals is considered to be the dominant sink for most

46 VOCs in the atmosphere, the ozonolysis and Cl atom reaction are also important removal processes

47 under certain environments [21-25]. It is recognized that O_3 is reactive towards certain classes of

48 organics, especially the unsaturated compounds, and ozonolysis process contributes to OH radical

49 and secondary organic aerosol formation [26]. Cl atom is also known to be extremely reactive towards

50 VOCs with most rate coefficients higher by an order of magnitude or more than that of OH radical [27,

51 28]. Cl-initiated photo-oxidation has been conventionally thought to be confined largely to the marine

52 boundary layer and heavily industrialized urban areas [29, 30]. However, recent field measurements of

53 anthropogenically derived photolabile Cl precursors ($ClNO_2$ and Cl_2) has presented evidence for Cl

54 chemistry in continental regions remote from coastal regions, which implies that the reactions of Cl

55 atom may contribute more to the tropospheric degradation of VOCs in the polluted mid-continental

56 regions [21, 31].

57   To date, the gas phase oxidations of MBO332 and MPO332 under atmospheric condition were

58 not fully understood. There were only few kinetic studies on MBO332 and MPO332, concerning the

59 rate constants for reactions of MBO332 and MPO332 with OH radical and NO_3 radical[32, 33]. In this

60 work, the first rate constants and products for the reactions of Cl atom and O_3 with MBO332 and

61 MPO332 were investigated with the purpose of more complete understanding of MBO332 and

62 MPO332 degradation processes in the atmosphere. The experiments were carried out in a simulation

63 chamber under NOx-free conditions at 293±1K and a total pressure of 1.01×10^5 Pa. The data were

64 used to estimate the atmospheric lifetimes and the potential environmental impacts, which have the

65 potential to increase the atmospheric chemistry database.

66 **Experimental Section**

67 **Smog chamber**

68   The experiments were conducted in a light-tight smog chamber, in which a 100 L FEP Teflon

69 film bag was housed as the reactor. More information of the chamber has been detailed in our

70 previous work[34, 35]. Briefly, the flexible Teflon chamber that maintains atmospheric pressure during

71 experiments was surrounded by a set of six UV fluorescent lamps (Philips TUV G1336W).

72 Temperature inside the chamber was regulated using a self-made temperature controller with an

73 accuracy of ±1 K for experimental conditions. An inlet and an outlet made of Teflon were used for

74 the introduction of reactants and gas sampling, and Teflon tubes were used to link the chamber and

75 analytical instruments. The liquid reactants were introduced into the chamber by flushing the carrier

76 gas through a 3-way glass tube which contained certain amount of compounds, warming where

77 necessary. A zero air gas generator (Thermo 111-D3R) was used to produce VOC-free air as carrier

78 gas for reactants and bath gas of the reactor, and a flow accumulator (D08-8C/ZM, Beijing Sevenstar

79 Electron Corporation) was used to record the total volume of the gas in the bag.

80 **Chemicals**

81   3-methyl-3-buten-2-one (TCI, 98%), 3-methyl-3-penten-2-one (Alfa Aesar, 95%), cyclohexane

82 (Alfa Aesar, 99+%), and dichlorosulfoxide ($SOCl_2$) (Alfa Aesar, 99+%) were used in this work.

83 Propene (1%, N_2 as bath gas), 1-butene (1%, N_2 as bath gas), O_2 (d＞99.999%), N_2 (d＞99.999%),

84 CO (50.6×10^{-6}, N_2 as bath gas) were supplied by National Institute of Metrology, China.

85 **Experimental Methods**

86 **Cl atom reactions**

87   The rate constants of MBO332 and MPO332 with Cl atom (k_K) were determined by using a

88 relative rate method, similar to our previous works [36], in which the ketones and the reference

89 compounds reacted with Cl atom (reaction (1) and (2)) and the consumption of the reactants were

90 monitored synchronously.

91   $$\text{ketones + Cl} \xrightarrow{k_K} \text{products} \qquad (1)$$

92   $$\text{reference + Cl} \xrightarrow{k_R} \text{products} \qquad (2)$$
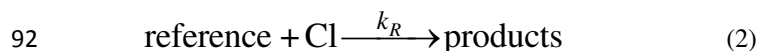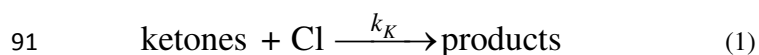
93   Where k_K and k_R were the rate constants for reactions (1) and (2) respectively. When combined

94 and integrated the rate equations for reactions (1) and (2), we could get the following equation

95   $$\ln\left(\frac{C_{K,0}}{C_{K,t}}\right) = \frac{k_K}{k_R}\ln\left(\frac{C_{R,0}}{C_{R,t}}\right) \qquad (\text{I})$$

96   Where $C_{K,0}$, $C_{K,t}$, $C_{R,0}$ and $C_{R,t}$ were the concentrations of ketones and references at time t_0 and t,

97 respectively. Providing that the reactions of ketones and reference compounds with Cl atom were the

98 only removal processes and none of them were reformed in any process. Therefore, a plot of

99 $\ln(C_{K,0}/C_{K,t})$ versus $\ln(C_{R,0}/C_{R,t})$ should be a straight line passing through the origin with the slope of

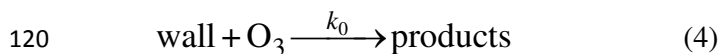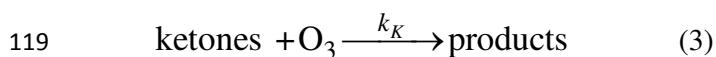100 k_K/k_R. Then k_K can be obtained through multiplying the slope by the known value of k_R.

101   Dichlorosulfoxide ($SOCl_2$) was used as a chlorine source, and Cl atoms were generated by in

102 situ photolysis of $SOCl_2$, with irradiation provided by the six UV fluorescent lamps with a maximum

103 intensity at 254 nm[37, 38]. Propene, 1-butene and cyclohexane were chosen as the reference

104 compounds because their Cl reaction rate constants were the same order of magnitude with the

105 expected rate constants of the studied unsaturated ketones.

106   The kinetic measurements were conducted in the air or N_2. The concentrations of the

107 unsaturated ketones and reference compounds were measured using a gas chromatograph equipped

108 with a flame ionization detector (GC/FID, GC6820, Agilent Technologies). Gas samples were

109 introduced via a 0.5mL Teflon loop mounted in a six way valve onto a DB-624capillary column (60

110 m length ×0.53 mm i.d., Agilent Technologies).

111   The initial concentrations of MBO332 and MPO332 were $(6.15\text{-}12.30)\times10^{14}$ and

112 $(5.28\text{-}10.56)\times10^{14}$ moleculecm^{-3}, respectively. Reference compounds were $(6.16\text{-}12.78)\times10^{14}$

113 molecule cm^{-3} and $SOCl_2$ was $(1.66\text{-}2.08)\times10^{15}$ molecule cm^{-3}.

114   **O$_3$ reactions**

115   The rate constants of the unsaturated ketones with O$_3$ were determined using an absolute rate

116   method[34, 39], in which the concentration of the unsaturated ketones was in large excess over that of

117   O$_3$, and can be regarded as a constant throughout the reactions essentially. The temporal profile of O$_3$

118   was governed by the following processes.

119    $$\text{ketones} + O_3 \xrightarrow{k_K} \text{products} \qquad (3)$$

120    $$\text{wall} + O_3 \xrightarrow{k_0} \text{products} \qquad (4)$$

121   In all experiments, the following equation could be obtained under pseudo-first-order

122   conditions.

123    $$-\frac{d\ln[O_3]}{dt} = k_0 + k_K[\text{ketones}]_0 \qquad (\mathrm{II})$$

124   Where k_K and k_0 were the rate constants for reactions (3) and (4). A plot of $-d\ln[O3]/dt$ against

125   [ketones] should be a straight line with k_0 intercept and slope of k_K, then k_K could be obtained through

126   this linear plot.

127   O$_3$ was produced by flowing oxygen through an ozone generator (BGF-YQ, Beijing Ozone,

128   China) into the chamber. O$_3$ concentration in the Teflon chamber was monitored by an ozone

129   analyzer (Model 49C, Thermo Electron Corporation, UV Photometric technology). Ketones were

130   introduced into the reactor followed by the addition of cyclohexane to scavenge any OH radical

131   formed during the reactions. Once O$_3$ was introduced, the chamber was connected to the ozone

132   analyzer and O$_3$ concentration were collected over 10s time intervals.

133   The initial O$_3$ concentration was in the range of $(2.46\text{-}4.92) \times 10^{12}$ molecule cm^{-3}, unsaturated

134   ketones concentrations were in the range of $(2.64\text{-}18.45) \times 10^{13}$ molecule cm^{-3}, and cyclohexane

135   concentration was about 1.68×10^{15} molecule cm^{-3}.

136   **Products analysis**

137   The products experiments were carried out in the chamber similar to the one described above,

138   except for the absence of reference compounds. The initial reactants concentrations were 2.46×10^{12}

139   molecule cm^{-3} approximately. Reactants and products were detected in real time using the

140   proton-transfer-reaction mass spectrum (PTR-MS) (IoniconAnalytik, HS PTR-QMS 500). PTR-MS

141   drift tube was operated at 2.2 mbar with a drift field of 600V cm^{-1}, and the E/N was 133 Td. The

142   temperatures of sample tube and drift tube were 60℃. Sampled air flow into the drift tube was

143   approximately 20 mL min^{-1}, while the water vapor flow was 7 mL min^{-1}.

144   The PTR-MS uses hydronium ions (H_3O^+) to chemically ionize the certain compound with a

145   proton affinity greater than that of water through an efficient proton transfer reaction. The protonated

146   organic ions can be detected based on mass to charge ratios (m/z) swiftly and sensitively.

147   Structurally different compounds with the same molecular weight cannot be distinguished from one

148   another, as compounds are identified by their molecular weight plus 1 (H^+). However, because the

149   nature of chamber experiments is controlled in the laboratory, where one ketone reacted with O_3 or

150   Cl atom at a time, the oxidation products will show increasing count rates with reaction time and can

151   be identified by the structure of the parent reactant through reasonable oxidation mechanisms. The

152   concentrations of compounds can be calibrated by the commercial standards or calculated using

153   known rate constants of the proton transfer reactions (See Electronic Supplementary Information for

154   calibration details of the PTR-MS).

155   **Result and Discussion**

156   **Rate constants of unsaturated ketones with Cl atom and O_3**

157   **Cl atom reactions.** Several control experiments concerning wall loss, photolysis and dark reactions

158   were performed before the kinetic measurements in order to verify the assumption that the reactants

159   were solely removed by the reactions with Cl atom. The mixtures of unsaturated ketones and

160   reference compounds were introduced into the chamber for the wall loss test in the absence of the Cl

161   atom precursor. Stable concentrations of the investigated compounds were monitored by GC-FID

162   through at least fifteen measurements over the course of 5 h, and the integrated peak areas decreased

163   were below 3% of their initial values. Then, the mixtures were subjected to photolysis for twice the

164   duration of each kinetic experiment without the Cl atom precursor. Moreover, Dark reactions were

165   carried out between the Cl atom precursor $SOCl_2$ and mixtures of unsaturated ketones and reference

166   compounds for the duration of each kinetic experiment. On the basis of the above experiments, it was

167   found that the loss caused by wall loss, photolysis and dark reactions could be negligible compared

168   to the loss occurred on conversion of the unsaturated ketones and reference compounds in the same

169   time span of the Cl atom reaction experiments. The reproducibility of these measurements were

170   obtained in the range 1–4%, and could be considered to be good.

171   The reactions of Cl atom with unsaturated ketones and reference compounds were carried out

172　individually to ensure the oxidation products do not interfere with the GC-FID measurements of

173　reactants. Therefore, propene, 1-butene and cyclohexane were used as reference compounds. The

174　typical logarithmic plots of the relative decrease in the form of Eq. (Ⅰ) for the reactions of Cl and

175　unsaturated ketones in the air are shown in Fig 1. As expected for relative rate plots, straight lines

176　with a zero intercept were obtained, indicating that the heterogeneous or secondary reactions were

177　insignificant. For each reference compound, the measurement was repeated for three times under

178　different initial concentration ratios of the ketones and reference compounds.

179　　　　　　　　　　　　　　　　　Fig1.

180　　　The rate constants ratio k_K/k_R and the obtained rate constants are summarized in Table 1. It

181　could be seen that O_2 had no much effect on the kinetic measurements. The average rate constants

182　were $(2.38\pm0.26)\times10^{-10}$ and $(3.00\pm0.34)\times10^{-10}$ $cm^3molecule^{-1}s^{-1}$ for MBO332 and MPO332, taken as

183　an average of all values. The listed errors consisted of twice the standard deviation from the

184　least-squares analysis of slope values and uncertainties of reference compounds rate constants.

185　　　　　　　　　　　　　　　　Table 1.

186　**O_3 reactions.** The loss of ozone for wall effect was also measured in the absence of ketones. The

187　background ozone decay was a first order reaction, and could be calculated as $k_0=3.23\times10^{-6}$ s^{-1},

188　which was about two orders of magnitude lower than the pseudo-first-order reaction rate constants in

189　the range of $(7.13-26.4)\times10^{-4}$ s^{-1} in this work. Therefore, the ozone loss caused by background decay

190　can be negligible.

191　　　　　　　　　　　　　　　　Table 2

192　　　For each reaction investigated, five runs were conducted in the case of different initial ketone

193　concentrations. The details were shown in the Table 2. In every experiment run, the decay of O_3

194　concentration was obtained as a function of time, and the decay rate of O_3 $(-dln[O_3]/dt)$ was yielded

195　by the slope of straight-line plot of $ln[O_3]_0/[O_3]_t$ against time $(t-t_0)$, as shown in Table 2 and Fig 2.

196　Then there were five decay rates of O_3 related to different unsaturated ketones concentrations for

197　each reaction investigated, and k_k was obtained through linear least-squares analysis of the plot of

198　decay rates of O_3 versus unsaturated ketones concentrations in the Fig 3. The rate constants for the

199　reactions of the unsaturated ketones with O_3 obtained were $(1.18\pm0.21)\times10^{-17}$ and $(4.07\pm0.45)\times10^{-17}$

200　$cm^3molecule^{-1}s^{-1}$ for MBO332 and MPO332, respectively. The errors given represented twice the

201　standard deviation from the least-squares analysis and about 10% of estimated systematic error.

202   Fig 2.

203   Fig 3.

204   Table 3 presents the rate constants for the reactions of the unsaturated carbonyl compounds with Cl

205   atoms and O_3, as well as their parent alkenes. The terminal methyl groups in parent alkenes were

206   replaced by -C(O)CH$_3$, -C(O)OCH$_3$ or –C(O)H to derive the carbonyl compounds. Intuitively, the

207   rate constants of MBO332 and MPO332 were found to be higher than those of 3-buten-2-one and

208   3-penten-2-one respectively, regardless of Cl reactions or O_3 reactions. It could be seen that the

209   reactivity of the unsaturated ketones increased due to increasing substitution at the carbon-carbon

210   double bond by methyl group, which was likely caused by the electron-donating inductive effect of

211   the methyl group directly attached to the double bond[33, 36, 40-43]. Due to the substitution of methyl

212   group in 3-buten-2-one and 3-penten-2-one, the reactivity of MBO332 and MPO332 were increased

213   by factors of 1.21 and 2.02 for reactions with Cl atom. Similarly, the reactivity of MBO332 and

214   MPO332 were increased by factors of 1.15 and 1.40 in O_3 reaction. The reactivity trend caused by

215   the substitution of methyl group was also applied to unsaturated esters and aldehydes, which could

216   be concluded from Table 3. The substitution of methyl group in methyl acrylate, methyl crotonate

217   and acrolein increased the reactivity of methyl methacrylate, methyl tiglate and methacrolein by

218   factors of 1.35, 1.04 and 1.13 in the Cl atom reactions, while the reactivity of methyl methacrylate,

219   methyl tiglate, methacrolein and trans-2-methyl-2-butenal were increased by factors of 7.17, 2.40,

220   4.15 and 3.38 in the O_3 reactions. The factors were different between the unsaturated ketones, esters

221   and aldehydes, which reflected that the different functional groups attached to the carbon-carbon

222   double bond also played important role on the reactivity of the unsaturated carbonyl compounds.

223   Table 3.

224   Intuitively, the unsaturated carbonyl compounds were all less reactive toward Cl atom and O_3

225   than the corresponding alkenes expect the reaction of acrolein with Cl atom, as seen in Table 3. This

226   reduction in reactivity showed the deactivating effect of the carbonyl group attached to the double

227   bond toward electrophilic reactions. For Cl atom reactions, the electron withdrawing effect of the

228   carbonyl group would lower the electron density on the double bond, and the rate constants were

229   reduced by the carbonyl group influencing Cl atom addition reaction. It was revealed that the

230   addition process to the carbon-carbon double bond played an important role in the unsaturated

231   ketones-Cl reactions. While the unsaturated ketones reacted with O_3, they were mainly initiated by

232 electrophilic addition of O_3 to the double bond [44], so the electron withdrawing effect of the carbonyl

233 group was also operational. However, the reduction of reactivity in Cl atom and O_3 reactions is

234 different for unsaturated ketones, esters and aldehydes.

235   The structure–activity relationships (SARs) developed by Atkinson[45] made the relation of the

236 reactivity of a compound to its chemical structure for predicting the rate constant. The

237 group-reactivity factors were often used to estimate the reactivity of groups of related compounds

238 that differ in their substitution concerning the reactions of unsaturated compounds[46, 47].

239
$$k_{SAR} = k_{basic} \prod_{i=1}^{4} C(x_i)$$

240 Where k_{basic} is the rate constant for the basic structure as the parent alkene mentioned above, and $C(x_i)$

241 were the group-reactivity factors that reflect the type of substituent attached to the double bond.

242   The group-reactivity factor for $-CH_3$ was taken as unity[48]. While the group-reactivity factors for

243 $-C(O)CH_3$, $-C(O)OCH_3$ and $-C(O)H$ for Cl atom reactions were calculated as 0.73, 0.74 and 0.87[47],

244 respectively, and those were 0.081±0.011, 0.070±0.017 for $-C(O)CH_3$ and $-C(O)OCH_3$ in O_3

245 reactions[49]. Then the experimental rate constants could be compared with the SAR calculated for

246 unsaturated carbonyl compounds, as shown in Fig 4.

247   Fig 4.

248   It can be seen that there was a good correlation between the experimental and the SAR calculated

249 rate constants for Cl atom reactions with an average ratio of k_{SAR}/k_{exp} 1.18. However, the ratios of

250 k_{SAR}/k_{exp} had large changes, which were in the range of 0.085-0.82 in reactions of unsaturated

251 ketones with O_3, and in the range of 0.78-2.78 for reactions of unsaturated esters with O_3.

252 **Products of unsaturated ketones react with Cl atom and O_3**

253 **Products identification.** PTR-MS was used to identify the products of each reaction by analyzing

254 the mass to charge ratio (m/z) of the product fragments.

255   When irradiation started, the typical variations of concentrations of MBO332, MPO332 and

256 products for the reactions with Cl atom as a function of time are illustrated in Fig 5. The m/z 31 and

257 93 were found to be dominant products in the reaction of MBO332 with Cl atom, identified as

258 formaldehyde (HCHO) and chloroacetone (CH3C(O)CH2Cl). While in MPO332, m/z45 and 107

259 assigned to be acetaldehyde (CH3CHO) and $CH_3C(O)C(O)Cl$ were the primary species, and m/z 31

260 and 87 having high yields in MPO332 showed the presence of HCHO and butanedione

261 (CH₃C(O)C(O)CH₃). Some products and patterns were consistently identified in the two reactions.

262 HC(O)Cl (m/z 54), CH₃C(O)Cl (m/z 79) and butanedione were observed in both reactions. Some

263 other products are detailed in the Table 3. CH₂=C(CH₃)C(O)CHO and CH₃CH=C(CH₃)C(O)CHO

264 from MBO332 and MPO332 showed decreases after they reached the peak (Fig 4 a-1 and b-1). We

265 inferred that they could have photodissociation reactions similar to methylglyoxal with irradiation

266 provided by UV fluorescent lamps[50, 51].

267 Fig 5.

268 Table 4.

269 Fig 6 shows the time series of MBO332 and MPO332 ozonolysis in the presence of excess of

270 CO as OH radical scavenger. In MBO332, the m/z 87 and m/z 31 were the main products assigned to

271 CH₃C(O)C(O)CH₃ and HCHO, together with the m/z 33, m/z 47 and m/z 75 corresponding to

272 CH₃OH, formic acid (HCOOH) and formic anhydride (HC(O)OC(O)H) with yields of (3±0.4)%,

273 (10±1)% and (5±0.5)%, respectively. CH₃C(O)C(O)CH₃ and CH₃CHO were identified as the

274 dominant products of MPO332 ozonolysis, and HCHO, CH₃OH, CH₂C(O) (m/z 43), CH₃C(O)OH

275 (m/z 61) and (CHO)₂ (m/z 59) as minor products. The signal at m/z 89 was observed by PTR-MS in

276 both O₃ reactions, and tentatively assigned to CH₃C(O)COOH.

277 Fig 6.

278 Table 4 and Table 5 summarize the formation yields of products detected in the reactions of

279 MBO332 and MPO332 with Cl atom and O₃. The product yields were calculated as the initial slopes

280 between increased concentrations of the oxidation products and decreased concentrations of the

281 studied ketones using the least squares regression method. Errors presented in Table 4 and Table 5

282 are twice the standard deviation from the least-squares analysis of the slopes and uncertainties

283 estimated in the PTR-MS calibrations. In reactions of Cl atom with MBO332 or MPO332, count

284 rates of CH₂=C(CH₃)C(O)CHO and CH₃CH=C(CH₃)C(O)CHO decreased after reaching the peak

285 with time, so only the data before the peak were used for the least squares regressions. For different

286 products having the same m/z, a total yield was applied, as compounds having a same m/z are

287 indistinguishable by PTR-MS. For O₃ reactions, the secondary consumption of products from

288 reactions with O₃ could be neglected. Whereas, the products may react with Cl atom in Cl atom

289 reactions. The corrections were made to the product yields to take into account the loss due to the

290 secondary reactions with Cl atom according to a method suggested by Atkinson et al (1982)[52]. In the

291 reaction of MBO332 with Cl atom, the correction factors were significant for formaldehyde, whereas

292 they were unimportant for chloroacetone. Taking into account the corrections, the yields of

293 formaldehyde and chloroacetone (including the Chlorine isotope effect) were 58±6% and 42±4%. In

294 the case of the reaction of MPO332 with Cl atom, the correction factors were important for

295 formaldehyde, acetaldehyde and methanol, and the yields with corrections were 47±5%, 58±6% and

296 3±0.2%, respectively.

297 Carbon balances of these reactions were all less than 1 and unclosed，which indicating that there

298 were oxidation products underestimated owing to their very low sensitivity or not to be detected by

299 PTR-MS. It could be seen that CO_2 and CO were important products in the Cl atom reactions from

300 the results obtained for methacrolein and methyl vinyl ketone[53]. However, they were not detected by

301 PTR-MS in our experiments, which is the significant carbon loss. If adding the similar level CO_2, the

302 carbon balances of MBO332 and MPO332 may be comparable to the literatures data. In addition, the

303 products losing in the tubing or partitioning into the particle phase also affected the close of carbon

304 balance.

305   Table 5.

306 **Reactions mechanisms.** In order to discuss the results conveniently, the reasonable product

307 structures and formation mechanisms for the reactions of MBO332 with Cl atom and O_3 were

308 proposed in Scheme1 and 2 based on the products identified above, respectively.

309 **MBO332 and MPO332 with Cl atom**

310 **MBO332** MBO332 reacted with Cl atom by addition to the carbon-carbon double bonds or H-atom

311 abstraction. The products of the suggested reaction pathways are $CH_3C(O)C(O)CH_3$(1), HC(O)Cl (2),

312 CH_2ClOH (3), $CH_3C(O)CH_2Cl$ (4), HCHO (5), CH_3OH (6) from Cl addition at the terminal carbon,

313 $CH_3C(O)Cl$ (7), $CH_3C(O)C(O)Cl$ (8), $CH_3C(O)C(CH_3)ClCH_2OH$ (9) and $CH_3C(O)C(CH_3)ClCHO$

314 (10) from the C2 addition and $C_5H_8O_2$ (11), $C_5H_6O_2$ (12) from H abstraction.

315 The Cl atom addition pathway could be divided into two sub-pathways depending on the position of

316 the added Cl atom. The initial addition would be followed by reaction with O_2 to form 1, 2- and 2,

317 1-chloroxyalkyl peroxy radicals [54]. In the present study, the1, 2- and 2, 1-chloroxyalkyl peroxy

318 radicals self-reactions would produce 1, 2- and 2, 1-chloroalkoxy radicals in the absence of NO,

319 respectively, while 2, 1-chloroxyalkyl peroxy radical also reacted with itself to form multifunctional

320 group compounds such as (9), (10). The alkoxy radicals were expected to react through four routes,

321 which included decomposition, reaction with O_2, isomerization through unimolecular or a

322 five-membered transition state [1]. The present work identified the possible reaction channels of the

323 chloroalkoxy radicals. The formation of chloroacetone (4) showed the major fate of 1,

324 2-chloroalkoxy radicals, cleavage of the C2-C3 bond to form (4) with a yield of $29\pm3\%$, (5) and (6).

325 The (1) (2) and (3) could be obtained in small yields by the cleavage of C1-C2 bond of the same

326 radical. It was in consistent with the results obtained for MAC and MVK observed by Orlando et al[53].

327 The chloroacetone from MAC and chloroacetaldehyde from MVK were also main products from the

328 scission of C2-C3 bond of the 1,2-chloroalkoxy radical from the Cl addition to the terminal carbon.

329 Orlando et al[53] have stated that elimination of CH_2Cl would not compete with $CH_3C(O)$ elimination

330 from the $CH_3C(O)CH(O\cdot)CH_2Cl$ radical in the MVK reaction, and methylglyoxal seems unlikely to

331 be produced. Similarly, the scission of C1-C2 bond of 1,2-chloroalkoxy radical in MBO332 reaction

332 also could be unimportant. For 2, 1-chloroalkoxy radicals, it could directly decompose to give

333 HCHO and chloroalkyl radicals, the latter decomposing into (7) or (8) in the presence of O_2 similar

334 to reaction pathways above, accompanied with the formation of HCHO or CH_3OH. The total yields

335 of HCHO (5) can be up to $(37\pm4)\%$.

336   H-abstraction reaction could happen on methyl of MBO332 to form $C_5H_8O_2$ (11), $C_5H_6O_2$ (12)

337 mentioned above, which were mixtures of the isomers. They were difficult to be distinguished from

338 one another by PTR-MS because of the isomers having the same m/z. The proposed structures are

339 given in Scheme1. Concerning the products yields mentioned in Table 3, it was indicated that Cl

340 atom addition reaction played a dominant role in reactions of unsaturated ketones with Cl atom,

341 especially Cl addition at the terminal carbon. While the H-abstraction process was of minor

342 importance.

343   Scheme 1.

344 **MPO332** A similar reaction mechanism and scheme for the reaction of MPO332 with Cl atom could

345 be expected (see ESI scheme SI). The CH3CHO with a yield of $58\pm6\%$ formed from the scission of

346 the C2-C3 bond bingding the alkoxy and carbonyl entities of the 3, 2-chloroalkoxy radical from the

347 Cl atom addition at the C3, accompanied with $CH_3C(O)Cl$, $CH_3C(O)C(O)Cl$, HCHO and CH_3OH.

348 The formation of $CH_3C(O)C(O)CH_3$ show that cleavage of the C2-C3 bond of the 2, 3-chloroalkoxy

349 radical was operative and accounted for 11%, which was from the Cl atom addition at the C2. The

350 decomposition of this radical also resulted in the production of the HC(O)Cl, $CH_3CHClOH$, HCHO

351 and CH_3OH. H-abstraction reaction could happen on methyl of MPO332 to form $C_6H_{10}O_2$ and

352 $C_5H_6O_2$, which were also mixtures of the isomers.

353 It could be interesting to give comparison on the products formed from the reactions of MBO332 and

354 MPO332 with Cl atom and those obtained for other unsaturated ketones, aldehydes and esters.

355 Orlando et al[53] have observed that chloroacetone as the main product with a yield of 42±5% formed

356 from scission of the C2-C3 bond binding the alkoxy and carbonyl entities of the 1,2-chloroalkoxy

357 radical from the Cl addition to the terminal carbon in methacrolein (MAC) oxidation process, and

358 HCHO with a yield of 18±2% was also observed. For methyl vinyl ketone (MVK),

359 chloroacetaldehyde and HCHO were the main products with yields of 75±8% and 47±7%, which

360 were also from scission of the C2-C3 bond of the 1,2-chloroalkoxy radical from the Cl addition to

361 the terminal carbon. However, Blanco et al. have observed that 1,2-chloroalkoxy radical formed in

362 the reaction of methyl methacrylate (MMA) could decompose to chloroacetone and HCHO with

363 yields of 41±6% and 35±5% by the scission of the C2-C3 bond, and HC(O)Cl and methyl pyruvate

364 from the cleavage of C1-C2 of the same radical were also observed with yields of 25±4% and

365 24±4%[55].

366 In the reaction of MBO332 with Cl atom, the main products were also from scission of the C2-C3

367 bond binding the alkoxy and carbonyl entities of the 1,2-chloroalkoxy radical from the Cl addition to

368 the terminal carbon, which was in consistent with the results obtained for MAC and MVK, but

369 contrasted with MMA. In the reaction of MPO332 with Cl atom, the products formed from the

370 decomposition of 3, 2-chloroalkoxy radical and 2, 3-chloroalkoxy radical due to the Cl atom addition

371 at the carbon-carbon double bond, which may result from the carbon-carbon double bond residing in

372 the middle of carbon chain of MPO332.

373 **MBO332 and MPO332 with O_3**

374 **MBO332** The reaction of MBO332 with O_3 proceeded by O_3 electrophilic addition on the double

375 bond and then leaded to the formation of the primary ozonide, which could rapidly decompose by

376 two channels [44], including (i) decomposing to give $CH_3C(O)C(O)CH_3$ and the Criegee intermediate

377 $[CH_2OO]^*$, and (ii) decomposing to give HCHO and Criegee intermediate $[CH_3C(O)C(CH_3)OO]^*$.

378 The least squares regression analysis described above gave yields of 30±3% and 44±5% for

379 $CH_3C(O)C(O)CH_3$ and HCHO, respectively. The both Criegee intermediates could undergo

380 collisional stabilization and react with various atmospheric trace gases. The excited forms were

381   proposed to have a number of decomposition and/or rearrangement pathways. For $[CH_2OO]^*$, it can

382   be stabilized, or decomposed to OH and some small molecules such as CO_2, CO. During the

383   reactions, HCOOH was formed in multiple reactions and detected in the experiments. Several

384   previous studies have indicated that formic anhydride (FAN) was produced in the decomposition of

385   hydroperoxy methyl formate (HPMF, $HOOCH_2OCHO$), a product of the reaction of stabilized

386   CH_2COO with HCOOH [56, 57]. Normally the formation of FAN should be observed subsequently to

387   the formation of HPMF. However, HPMF (m/z 93) was not observed in our experiment under the

388   conditions of excess CO as OH scavenger. The formed FAN was possibly resulted from the reaction

389   of dioxirane with CO, as shown in scheme 2[58].

390   Scheme 2.

391   **MPO332** The primary ozonide rapidly decomposed to $[CH_3CHOO]^*$ and $CH_3C(O)C(O)CH_3$,

392      $[CH_3C(O)C(CH_3)OO]^*$ and CH_3CHO. The formation yields of $CH_3C(O)C(O)CH_3$ and CH_3CHO

393   were 39±4% and 61±7%. $[CH_3CHOO]^*$ could directly decompose to OH radicals and HCHO,

394   CH_3OH etc. Moreover, it may lead to the corresponding carboxylic acid ($CH_3C(O)OH$), or rearrange

395   to the corresponding unsaturated hydroperoxide ($CH_2=CHOOH$), which form OH and an alkoxy

396   radical, which could undergo isomerization or decomposition to form CH_2OHCHO (m/z 61), glyoxal

397   (m/z 59) and HCHO (see ESI scheme S2). CH_2OHCHO (m/z 61) had the same m/z as $CH_3C(O)OH$,

398   and they cannot be distinguished by PTR-MS in this work.

399   Up to now, the fate of $[CH_3C(O)C(CH_3)OO]^*$ has not been elucidated, which was produced in

400   both MBO332 and MPO332 when reacted with O_3. Some possible reaction pathways of the Criegee

401   intermediate are given in scheme 2. The intermediate couldn't generate OH radical in the

402   decomposition of the energy-rich hydropeoxide formed by isomerization, as there was no

403   observation of the products from the decomposition of the hydroperoxide. $[CH_3CH_2C(O)CHOO]^*$,

404   similar to the Criegee intermediate in this work, has been reported to lead to the carboxylic acid

405      $CH_3CH_2C(O)COOH$ [59]. Therefore, it was possible for $[CH_3C(O)C(CH_3)OO]^*$ to form

406      $CH_3C(O)COOH$, which may be demonstrated by the detection of the signal m/z 89 using PTR-MS.

407   A decomposition pathway may also happen to give the formations of CO_2 and some other radicals,

408   such as CH_3 and $CH_3C(O)$, which could lead to HCHO or CH_3OH.

409   **Conclusion and Atmospheric implications**

410   On the basis of rate constants obtained in this work, the atmospheric lifetimes of the unsaturated

411 ketones with respect to reactions with Cl atoms and O_3 are calculated using the formula:$\tau=1/(k\cdot[X])$,

412 in which [X] represents the concentration of typical atmospheric oxidants (OH, NO_3, Cl and O_3) and

413 k is the rate constant of the reactions between the oxidants and the considered ketones. The relative

414 importance of Cl atom and O_3 can be estimated compared to the reactions with OH and NO_3 radicals.

415   Table 5.

416   The tropospheric lifetimes for unsaturated ketones due to reaction with OH radicals are in the

417 range of a few hours and thus represent the dominant atmospheric sink process, indicating that these

418 compounds will be degraded close to their emission sources. Lifetimes of the ketones based on Cl

419 atom reactions are much longer than these based on OH radical. Nevertheless, in the marine

420 boundary layer and coastal areas, the peak concentration of Cl atom reaches as high as 10^5 molecule

421 cm^{-3} in early morning, and then Cl based lifetimes turn to 11 h and 9 h for MBO332 and MPO332,

422 respectively. Cl atom reactions may have the potential to compete with OH-initiated reactions.

423 Therefore, Cl-initiated reactions may play an important role in the degradation of the studied ketones.

424 As mentioned in the introduction, recent field measurements have presented strong evidences for

425 $ClNO_2$ mediated Cl atom chemistry in continental regions. The Cl atom reactions may play a more

426 significant part in atmospheric chemistry than previously thought, although the distribution of these

427 sources remains to be established in the future. Similarly, the lifetimes due to O_3 reactions would

428 turn to 8 h and 2 h for MBO332 and MPO332 respectively in some urban areas with elevated O_3

429 levels reaching up about 4.57×10^{12} molecule cm^{-3} [60]. Therefore, the O_3 reaction may be a

430 considerable homogeneous removal process for the studied ketones too.

431   In the light of our results, the reactions of unsaturated ketones with Cl atom and O_3 mainly lead

432 to the formation of formaldehyde, acetaldehyde and chloroacetone, which are pollutants involved in

433 photochemical smog or health effect. And other highly oxygen-containing compounds such as

434 $CH_3C(O)C(O)Cl$ and butanedione may be expected to be precursors of organic aerosol. Moreover,

435 the chlorinated products are also the potential approach to be served as the specific chlorine atom

436 precursors in the Cl-initiated chemistry in the troposphere [61]. To the best of our knowledge, this is

437 the first report on the kinetics and products analysis for the reactions of MBO332 and MPO332 with

438 Cl atom and O_3 in the absence of NOx. However, under the conditions prevailing in the urban areas,

439 NOx will be involved in the oxidation reactions of unsaturated ketones. More information about the

440 products and mechanisms of these particular reactions has to be acquired based on different

441 atmospheric conditions to evaluate their atmospheric importance.

442 **Acknowledgments**

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560 Table 1. Summary of rate coefficient ratios k_S/k_R and rate coefficients for reactions of Cl atoms with
561 unsaturated ketones in the air and N_2 at room temperature and atmospheric pressure

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VOCs	Reference	Carrier gas	$^a k_K/k_R$	$^b k_S$ $(10^{-10} cm^3 molecule^{-1} s^{-1})$	$\overline{k_K}$
3-methyl-3-buten-2-one （MBO332）	Propene	air	0.96±0.01	2.21±0.29	2.38±0.26
		N$_2$	0.93±0.003	2.14±0.28	
	1-Butene	air	0.78±0.01	2.34±0.31	
		N$_2$	0.73±0.01	2.19±0.29	
	Cyclohexane	air	0.74±0.01	2.59±0.19	
		N$_2$	0.81±0.01	2.83±0.21	
3-methyl-3-penten-2-one (MPO332)	Propene	air	1.20±0.01	2.76±0.36	3.00±0.34
		N$_2$	1.16±0.01	2.67±0.35	
	1-Butene	air	0.95±0.02	2.85±0.39	
		N$_2$	1.10±0.01	3.3±0.44	
	Cyclohexane	air	0.90±0.01	3.15±0.23	
		N$_2$	0.94±0.02	3.29±0.25	

562   a.The errors represent 2σ.

563   b Rate coefficients at 298 K used for the reactions of Cl with propene, 1-butene, and cyclohexane were (2.3±0.3)×10^{-10} cm^3

564   molecule^{-1} s^{-1} [62], (3.0±0.4)×10^{-10} cm^3 molecule^{-1} s^{-1} [53], and (3.5±0.25)×10^{-10} cm^3 molecule^{-1} s^{-1} [45], respectively.

565   Table 2. The experimental conditions and results from the reactions of O$_3$ with MBO332 and
566   MPO332 using the absolute method

ketone	[ketone] 10^{13} molecule cm^{-3}	[O$_3$]$_0$ 10^{12} molecule cm^{-3}	[cyclohexane] 10^{15} molecule cm^{-3}	-dln[O$_3$]/dt 10^{-4} s^{-1}
3-methyl-3-buten-2-one (MBO332)	6.15±0.12	2.78	1.68	7.13±0.01
	9.23±0.18	3.02	1.68	11.0±0.04
	12.3±0.24	3.68	1.68	14.5±0.03
	15.4±0.30	3.22	1.68	18.2±0.05
	18.5±0.36	2.89	1.68	21.5±0.04
	$k_{MBO332+O3}$=(1.18±0.21) ×10^{-17} cm^{3}molecule^{-1}s^{-1}			
3-methyl-3-penten-2-one (MPO332)	2.69±0.09	2.06	1.68	10.8±0.01
	3.22±0.10	2.18	1.68	13.3±0.02
	4.30±0.12	3.23	1.68	17.3±0.02
	5.37±0.15	2.29	1.68	21.7±0.02
	6.44±0.18	3.12	1.68	26.4±0.05
	$k_{MPO332+O3}$=(4.07±0.45) ×10^{-17} cm^{3}molecule^{-1}s^{-1}			

567   Table 3. Rate constants for the gas-phase reaction of unsaturated carbonyl compounds with Cl atom
568   and O3 and their parent alkenes.

Unsaturated ketones	k (cm^{3}molecule^{-1}s^{-1})		Parent alkenes	k (cm^{3}molecule^{-1}s^{-1})	
	Cl atom(10^{10})	O$_3$(10^{18})		Cl atom(10^{10})	O$_3$(10^{17})
3-buten-2-one CH$_2$=CHC(O)CH$_3$	1.95±0.52[63]	5.84±0.39[59]			
methyl acrylate CH$_2$=CHC(O)OCH$_3$	1.71±0.13[65]	0.95±0.07[66]	1-propene	2.30±0.30[62]	1.06±0.12[64]
acrolein CH$_2$=CHCHO	2.53±0.72[63]	0.26±0.05[67]			
3-methyl-3-buten-2-one CH$_2$=C(CH$_3$)C(O)CH$_3$	2.38±0.26[a]	11.8±2.10[a]			
methyl methacrylate CH$_2$=C(CH$_3$)C(O)OCH$_3$	2.30±0.18[65]	6.70±0.90[66]	isobutene	3.40±0.28[29]	1.24±0.08[68]
methacrolein CH$_2$=C(CH$_3$)CHO	2.86±0.76[63]	1.08±0.20[59]			
3-penten-2-one CH$_3$CH=CHC(O)CH$_3$	2.53±0.54[70]	29.5±4.10[70]			
methyl crotonate CH$_3$CH=CHC(O)OCH$_3$	2.21±0.17[65]	4.38±0.30[67]	(E)-2-butene	3.31±0.47[29]	23.8±1.5[64]
crotonaldehyde CH$_3$CH=CHCHO	3.16±0.93[63]	1.58±0.23[70]			
3-methyl-3-penten-2-one CH$_3$CH=C(CH$_3$)C(O)CH$_3$	3.00±0.34[a]	40.7±4.50[a]			
methyl tiglate CH$_3$CH=C(CH$_3$)C(O)OCH$_3$	2.92[72]	10.5[72]	2-methyl-2-butene	3.95±0.32[29]	41.0±5.0[71]
trans-2-methyl-2-butenal CH$_3$CH=C(CH$_3$)CHO	/	5.34±0.73[70]			

569   [a] This work.

570   Table 4. Formation yields of products during experiments of MBO332 and MPO332 with Cl atom

Products of MBO332+Cl	Yield (%)	Products of MPO332+Cl	Yield (%)
HCHO	58±6 [b]	CH$_3$CHO	58±6 [b]
Chloroacetone	42±4 [c]	CH$_3$C(O)C(O)Cl	14±2
2,3-Butanedione	3±0.32	HCHO	47±5 [b]
CH$_3$OH	2±0.22	2,3-Butanedione	11±2
HC(O)Cl	1±0.11	CH$_3$OH	3±0.2 [b]
CH$_2$ClOH	≈0.2	CH$_3$C(O)Cl	≈0.4
CH$_3$C(O)C(O)Cl	≈0.4	HC(O)Cl	1±0.14
CH$_3$C(O)Cl	≈0.4	CH$_3$CHClOH	≈0.2
CH$_2$=C(CH$_3$)C(O)CHO	4±0.3[a]	CH$_3$CH=C(CH$_3$)C(O)CHO	3±0.5[a]

$CH_2=C(CH_3)C(O)CH_2OH$	3 ± 0.2^a	$CH_3CH=C(CH_3)C(O)CH_2OH$	$\approx0.8^a$
$CH_3C(O)CCl(CH_3)CHO$	≈0.2		
$CH_3C(O)CCl(CH_3)CH_2OH$	≈0.07		
Carbon balance (%)	48 ± 5	Carbon balance (%)	46 ± 6

571 ^{a}The yields included mixtures of the isomers

572 ^{b}The yields including the corrections from secondary reaction with Cl atom

573 ^{c}The yields including the corrections from secondary reaction with Cl atom and the the Chlorine isotope effect

574 Table 5. Formation yields of products during experiments of MBO332 and MPO332 ozonolysis in

575 the presence of excess CO

Products of MBO332+O_3	Yield (%)	Products of MPO332+O_3	Yield (%)
HCHO	44 ± 5	CH_3CHO	61 ± 7
2,3-Butanedione	30 ± 3	2,3-Butanedione	39 ± 4
HCOOH	10 ± 1	HCHO	15 ± 2
CH_3OH	3 ± 0.4	CH_3OH	3 ± 0.5
Formic anhydride	5 ± 0.5	CH_2CO	21 ± 2^a
pyruvic acid	<0.01	Glyoxal	5 ± 1
		$OHCCH_2OH$	7 ± 1^b
		pyruvic acid	1 ± 0.2
Carbon balance (%)	38 ± 4	Carbon balance (%)	61 ± 7

576 ^{a} included the signal of $OHCCH_2OH$ (m/z 61) eliminating one H_2O molecule

577 ^{b} included the signal of $CH_3C(O)OH$ (m/z 61)

578 Table 6. Summary of rate constants and estimated atmospheric chemical lifetimes τ for the reactions

579 of unsaturated ketones with OH, NO_3, Cl, and O_3.

Molecule	k(cm^3 molecule^{-1} s^{-1})				τ(h)			
	$k_{OH}\times10^{11}$	$k_{O3}\times10^{17}$	$k_{NO3}\times10^{15}$	$k_{Cl}\times10^{10}$	τ_{OH}(h)	τ_{O3}(h)	τ_{NO3}(h)	τ_{Cl}(h)
3-methyl-3-buten-2-one (MBO332)	3.60^b	1.18^c	8.27^d	2.38^c	3.86	33.63	67.18	116.71
3-methyl-3-penten-2-one (MPO332)	4.20^b	4.07^c	155^d	3.00^c	3.31	9.75	3.58	92.59

580 ^{a}The concentrations of OH, NO_3, O_3 and Cl used in the calculations are 2×10^6 molecules cm^{-3} , 5×10^8 molecules cm^{-3} , 7×10^{11}

581 molecules cm^{-3}[39], and 1.0×10^4 molecules cm^{-3},[73], respectively.

582 ^{b}Rate coefficients of OH radical reactions[32]

583 ^{c}Rate coefficients of O_3 and Cl atom reactions: This work.

584 ^{d}Rate coefficients of NO_3 radical reactions[33]

585

586 Figure captions

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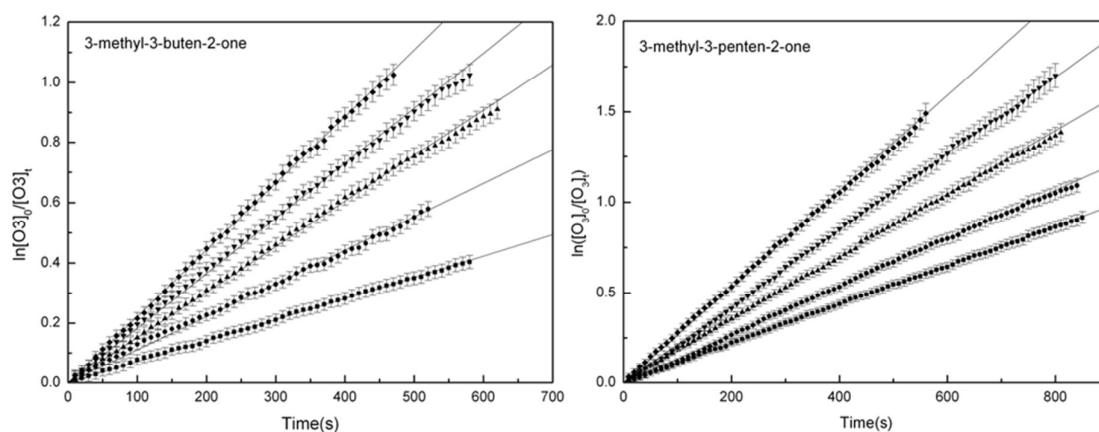
587   Fig 1. Relative loss of MBO332 and MPO332 versus reference compounds in presence of Cl atoms

588   Fig 2. Pseudo-first-order plots for O_3 reactions with different concentrations of (a) MBO332 and (b)

589   MPO332

590   Fig 3. Plots of $-d\ln[O_3]/dt$ versus ketones concentrations

591   Fig 4. Comparisons of the experimental and SAR calculated rate constants for reactions of

592   unsaturated carbonyl compounds with Cl atom and O_3.

593   Fig 5. Reaction products of Cl atom with (a) MBO332 and (b) MPO332

594   Fig 6. Products for O_3 reactions with (a) MBO332 and (b) MPO332

595   Scheme 1. Proposed Reaction pathways for the reaction of MBO332 with Cl atom

596   Scheme 2. Proposed reaction pathways of MBO332 with O_3

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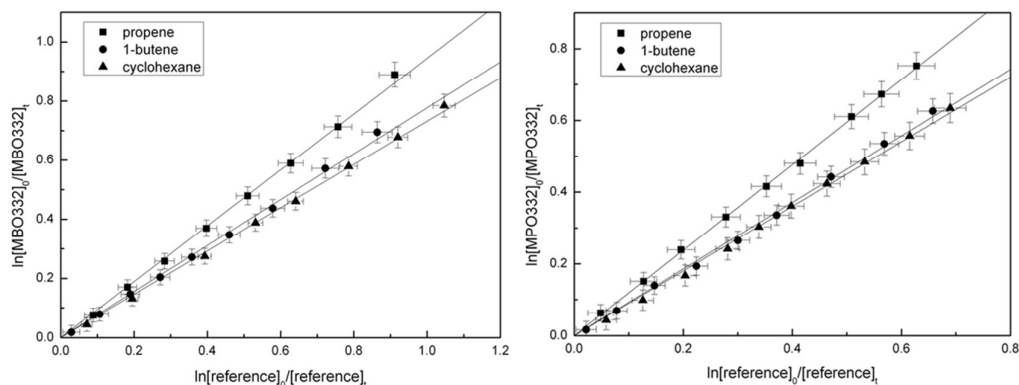
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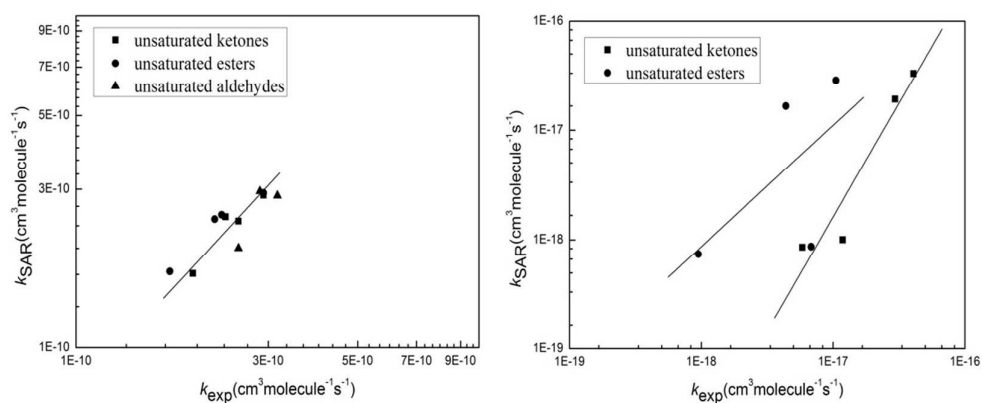
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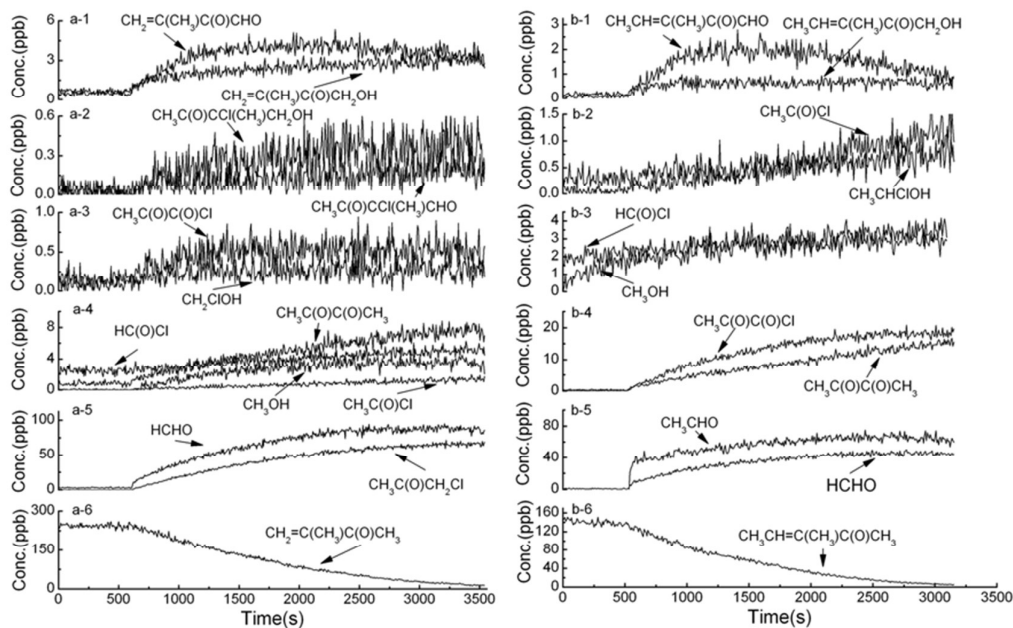
603   MPO332
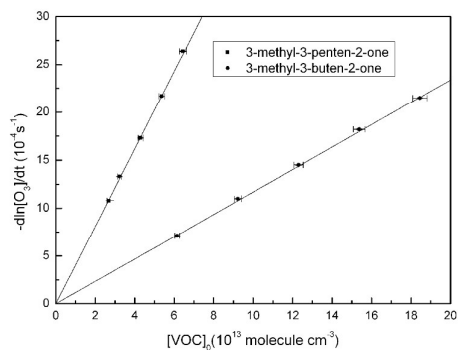
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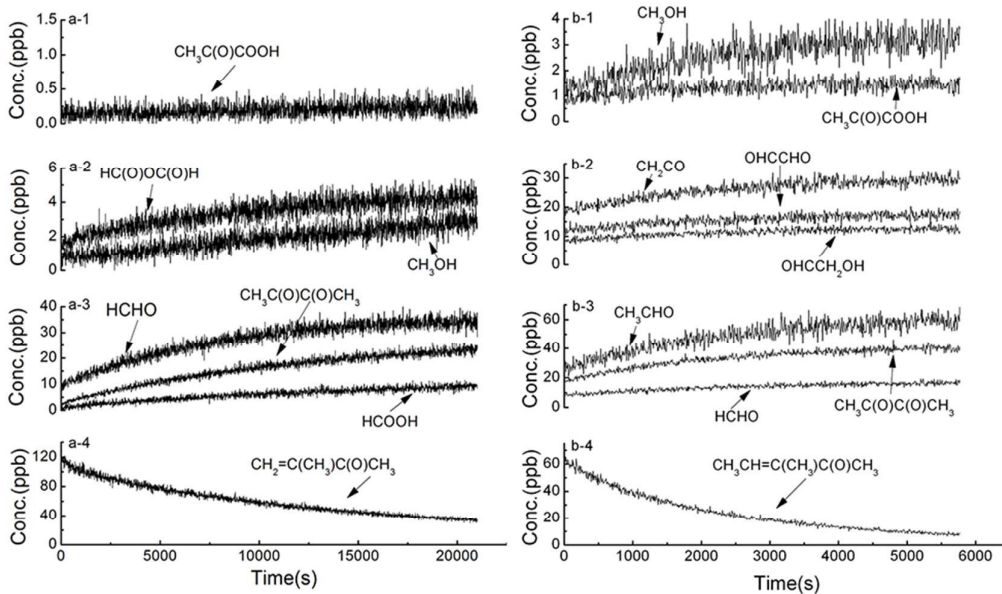
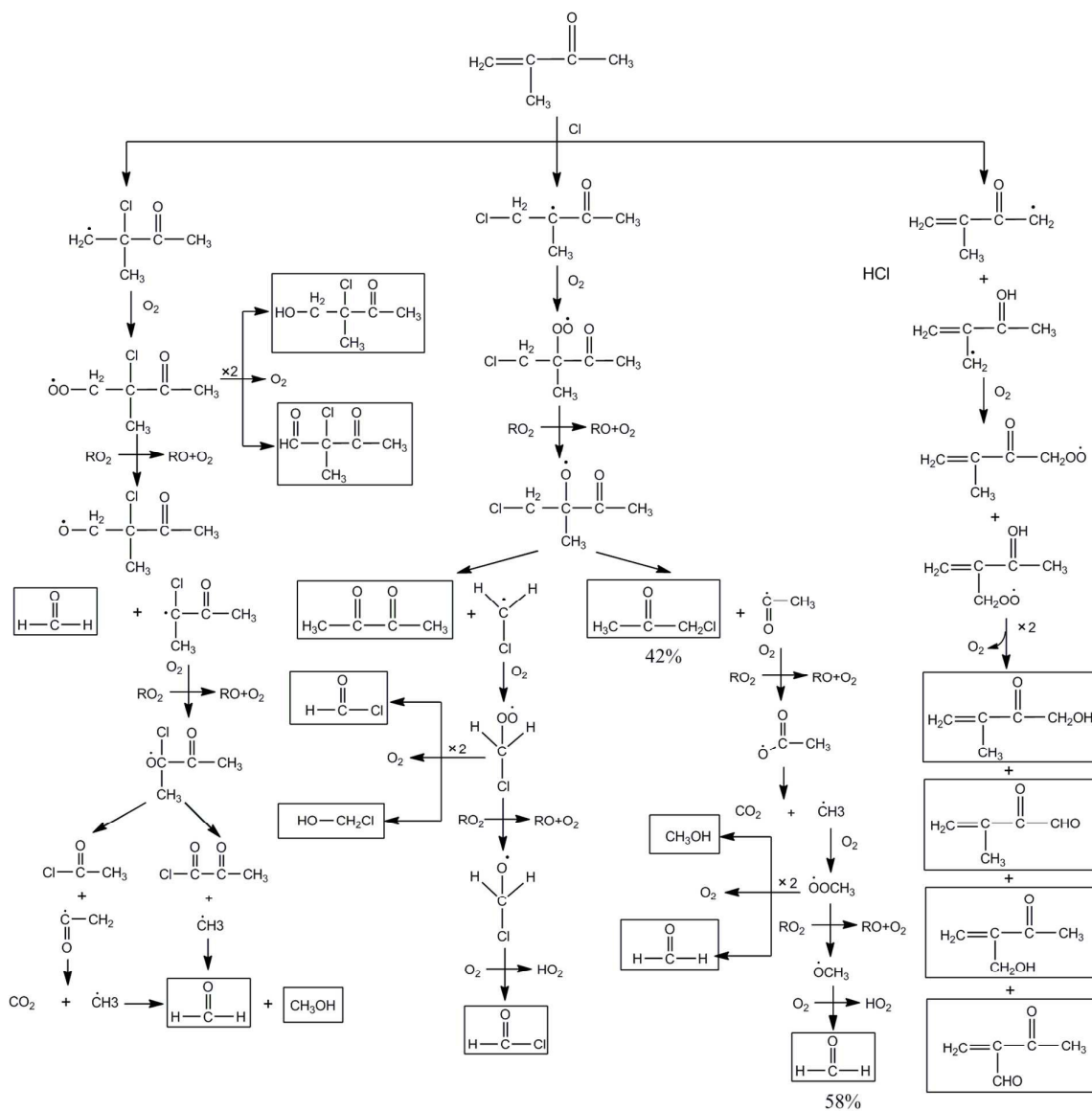608   unsaturated carbonyl compounds with Cl atom and O_3.

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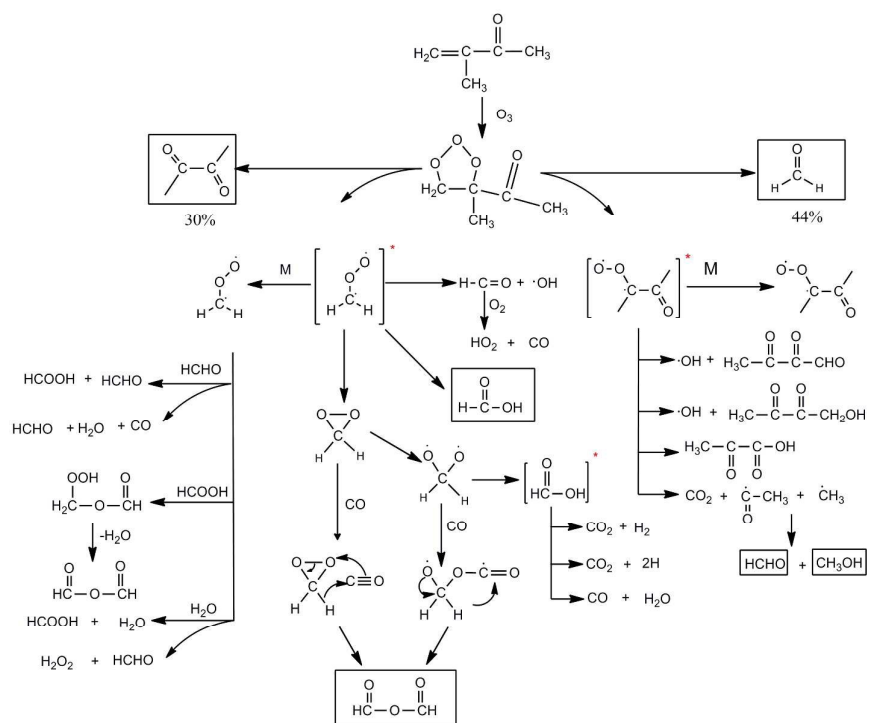610   Fig 5. Reaction products of Cl atom with (a) MBO332 and (b) MPO332

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