Chemical Physics Letters 472 (2009) 23-29

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

CHEMICAL PHYSICS LETTERS

Methyl acetate reaction with OH and Cl: Reaction rates and products for a biodiesel analogue

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ARTICLE INFO

Article history: Received 20 August 2008 In final form 23 February 2009 Available online 27 February 2009

ABSTRACT

Relative rate experiments performed in a photochemical reactor at 293 \pm 0.5 K and a total air pressure of 980 mbar were used to determine $k(CH_3C(O)OCH_3 + CI) = (1.93 \pm 0.27) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(CH_3C(O)OCH_3 + OH) = (3.18 \pm 0.13) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The product branching ratio for the Cl-initiated oxidation of CH₃C(O)OCH₃ was investigated at 293 \pm 0.5 K and 980 mbar N₂, air, or O₂, in the presence and absence of NO. Products observed were CH₃C(O)OCHO, CH₃C(O)OH, HC(O)OH, CO, and CO₂. The product branching ratios were dependent on NO, but not on the oxygen partial pressure. © 2009 Elsevier B.V. All rights reserved.

1. Introduction

The production and use of transportation biofuels has grown rapidly during the last decade due to the desire to reduce carbon dioxide emissions and dependence on oil. In addition to the carbon budget, biofuel production and use can involve emission of greenhouse gases such as N₂O due to use of fertilizer [1], and the use of ethanol blends may increase the concentration of atmospheric pollutants including formaldehyde and acetaldehyde [2]. Production of biodiesel has been commercially important since the beginning of the 1990's. From 2001 to 2006 the global production of biodiesel expanded six fold. In 2006, 73% of global biodiesel was produced in Europe with rapeseed and sunflower being the major sources [3,4].

Biodiesel consists of methyl esters derived from plant oils, which are long-chain fatty acids such as methyl oleate [5]. When used in engines, incomplete combustion leads to the formation of a variety of chemical compounds in the exhaust. In addition, an estimated 0.01–0.1% of all transportation fuel is emitted directly to the atmosphere [6]. Combustion products from biodiesel include shorter chained methyl esters, aldehydes, and methyl acrylates [7,8].

In order to assess the environmental impact of biofuels, life cycle analysis of the fuels must be carried out. The last step of the life cycle involves combustion of the fuel. In the present work, the atmospheric fate of a short chained methyl ester, used as an analogue to uncombusted biodiesel compounds, has been investigated. An important component of a compound's environmental impact is its lifetime in the atmosphere. This can be estimated from the reaction rate of the compound with key oxidants. In ambient air the most important reactive species is the hydroxyl radical which is present at a concentration of approximately 1×10^6 radicals cm⁻³ [9].

Another atmospheric oxidant is the chlorine atom. The most important source of Cl is photolysis of chlorine containing species in sea salt aerosols [10]. Reaction mechanisms involving Cl are similar to those of the OH-radical, with rate constants 10–100 times larger than for the corresponding OH-reactions. Therefore, also due to their ease of production in the laboratory, it is useful to use Cl-atom initiated reactions as models for OH-radical initiated reactions. In the atmosphere, oxidation by Cl atoms may be important in the marine boundary layer where peak concentrations have been observed to be 10^3 – 10^6 cm⁻³ [11].

In this study methyl acetate has been used as a model for biodiesel. This short chained compound has a relatively high vapor pressure for a methyl ester, and is therefore feasible for study in the laboratory. The reactivity of methyl acetate with OH and Cl has been studied in the presence of varying concentrations of oxygen and in the presence and absence of NO_x . For the Cl reaction the product distributions given various conditions have been determined.

There are three previous studies of the rate constant for the reaction of methyl acetate with Cl published in the literature, and the details for these are given in Table 2. The product branching ratio for the reaction has been determined in the presence and absence of NO with varying oxygen partial pressures [12], and the temperature dependence of this branching ratio was studied by Tyndall et al. in the temperature range 253–324 K, in the absence of NO, and at a total pressure of 910 mbar with varying oxygen partial pressures [13].

There are four previous studies of the rate constant for the reaction of methyl acetate with OH, which are summarized in Table 2. The product branching ratio of the OH-initiated oxidation of methyl acetate at 296 K has been determined in the presence of



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NO and at a total pressure of 910 mbar with varying oxygen partial pressures by Tyndall et al. [13].

We have undertaken the present study using the new photochemical reactor in Copenhagen to further investigate the reaction rate and the reaction products. Differences between the results of the present study and previous studies will be discussed.

2. Experimental setup

The experimental system used in this work is described elsewhere [14] and is summarized here. The system consists of a 100 L quartz reaction chamber sealed in both ends with stainless steel flanges and surrounded by eight UV-A, sixteen UV-C, and twelve broadband sun lamps. The system is enclosed in an insulating box equipped with a temperature control system to ensure stable (within 0.5 K) temperatures during experiments. Reactants are introduced into the chamber using a pyrex gas handling manifold with a calibrated volume. By monitoring the pressure of the calibrated volume, the concentrations of the compounds introduced into the chamber can be determined.

The reactions in the chamber were monitored with a Bruker IFS 66v/s FTIR spectrometer. An absorption path length of 72 m was obtained using a White type optical system in the reaction chamber. A liquid nitrogen cooled MCT detector with a range of 12000– 850 cm^{-1} was used, and IR spectra at a resolution of 0.125 cm⁻¹ were obtained by co-adding 64 interferograms.

3. Materials and methods

Methyl acetate was reacted with OH and Cl radicals in the photochemical reactor, in order to determine the following reaction rates:

$$\begin{array}{ll} CH_3C(0)OCH_3+Cl \rightarrow products & (1) \\ CH_3C(0)OCH_3+OH \rightarrow products & (2) \end{array}$$

The reaction rates were determined relative to two reference reactions. In the Cl experiment both references were present at the same time in each experiment, whereas in the OH experiment only one reference was present at a time. The reference reactions were the following:

$C_2H_5Cl + Cl \rightarrow products$		3
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 $CH_3Br + Cl \rightarrow products \tag{4}$

 $C_2H_4F_2 + OH \rightarrow products \tag{5}$

$$C_2H_6 + OH \rightarrow products$$
 (6)

Rate constants for the reference reactions are given in Table 1. k_1 was determined relative to k_3 and k_4 , and k_2 was determined relative to k_5 and k_6 . In order to establish the reliability of the experimental system, k_3 was determined relative to k_4 and k_5 was determined relative to k_6 in separate experiments.

The following chemicals were used: $CH_3C(O)OCH_3(\ge 99\%, Rie$ del-de Häen), C_2H_5Cl ($\ge 99.7\%$, Gerling Holz + CO), CH_3Br (99%, Gerling Holz + CO), C_2H_6 ($\ge 99.95\%$, Fluka), CH_2FCH_2F ($\ge 99\%$, [15]).

Initial concentrations of reactants were in the range 9–43 ppm. For the Cl experiments initial C₂H₅Cl and CH₃Br concentrations

 Table 1

 Rate constants for the reference compounds used in this work.

Reaction	Rate constant	Ref.
$\begin{array}{l} (3) \ C_2H_5Cl+Cl \rightarrow products \\ (4) \ CH_3Br+Cl \rightarrow products \\ (5) \ C_2H_4F_2+OH \rightarrow products \\ (6) \ C_2H_6+OH \rightarrow products \end{array}$	$\begin{array}{l} (8.7\pm1.0)\times10^{-12}cm^3molecule^{-1}s^{-1} \\ (4.29\pm0.35)\times10^{-13}cm^3molecule^{-1}s^{-1} \\ (8.78\pm0.88)\times10^{-14}cm^{-3}molecule^{-1}s^{-1} \\ (2.27\pm0.93)\times10^{-13}cm^3molecule^{-1}s^{-1} \end{array}$	[28] [29] [30] [31]

were 7–71 ppm and 128–158 ppm, respectively. For the OH experiments reference concentrations were 29–58 ppm. The total pressure of the reaction mixture in each experiment was 980 mbar and the temperature was 293 ± 0.5 K. For the relative rate experiments, technical air (21% O_2 and 79% N_2) was used as the background gas. The product study was done in 980 mbar N_2 , 980 mbar technical air and 980 mbar O_2 . The reaction in N_2 was carried out in the absence of NO, the reaction in technical air was carried out both in the presence and absence of NO. The reaction in O_2 was carried out in the presence of NO. This was done in order to determine the oxygen- and NO-dependence of the reaction yields. In these experiments initial methyl acetate and NO concentrations were in the range 25–45 ppm.

UV-A light with a maximum emission wavelength of 350 nm was used to generate Cl atoms from Cl_2 gas in the reaction chamber. A concentration of Cl_2 of approximately five times the total concentration of reactants (methyl acetate and reference compounds) was used. One UV-A lamp was used and the photolysis was performed in the presence of all compounds at time intervals of 2 s to 5 min. After each photolysis step an IR spectrum was recorded.

For the generation of OH radicals a mixture of O_3 and H_2O was irradiated with four UV-C lamps in the presence of both reactants in the chamber. O_3 was generated from O_2 with an ozone generator, and condensed on a silica gel that was cooled with ethanol and dry ice to ca. -70 °C. The initial concentration of ozone and water vapour was approximately 20 and 10 times the total concentration of reactants, respectively. The photolysis steps in the OH-experiments were between 5 s and 10 min, and after each photolysis step an IR spectrum was recorded. Each experiment was performed twice in order to check reproducibility. The resultant relative rate plots include data from the two identical experiments. Calibrated reference spectra of the studied reactant, reference compounds, and a number of the possible products were recorded in the same reaction chamber and under the same conditions as the experiments.

The reaction rates were determined using the relative rate method. This method assumes that the investigated reaction is the only significant loss process for the reactant and references and that these compounds are not formed in the chamber. The following relation is then valid:

$$\ln\left(\frac{[\text{reactant}]_0}{[\text{reactant}]_t}\right) = \frac{k_{\text{reactant}}}{k_{\text{reference}}} \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right)$$

where $[reactant]_0$ and $[reference]_0$ are the initial concentrations of reactant and reference, respectively, and $[reactant]_t$ and $[reference]_t$ are the concentrations of reactant and reference at time *t*. Plotting $ln\left(\frac{[reactant]_0}{[reactant]_t}\right)$ versus $ln\left(\frac{[reference]_0}{[reference]_t}\right)$ gives a straight line with slope: $\frac{k_{reactant}}{k_{reference}}$ [16]. The errors for the reported rate constants are computed from the standard error on the slope of the relative rate plot. Errors on the relative rate plots are in the order of 0.5–5%.

4. Relative rate results

To test for possible photolytic breakdown, methyl acetate and the reference compound in air were irradiated in separate experiments under the same conditions (number of lamps and time span) as a typical relative rate experiment. The tests were performed both with one UV-A lamp with a spectral range of 320–380 nm and with 4 UV-C lamps with emission at 254 nm. The time span was typically 20 minutes. The tests showed no photolysis of the compounds. To examine any dark reactions that might occur, mixtures of methyl acetate, the two reference compounds and chlorine in air were left for 10–30 min in the chamber with no lights on. A



Fig. 1a. Relative rate plots for the CI-reaction of methyl acetate at 293 K and a total air pressure of 980 mbar.

similar test was performed in the presence of ozone and water vapour. No significant evidence of dark reactions was seen.

4.1. Cl-experiments

For the reaction of methyl acetate with chlorine, C_2H_5Cl and CH_3Br were used as reference compounds. C_2H_5Cl concentrations were determined using the strong absorption peak at 1289 cm⁻¹ and CH_3Br concentrations were determined using the absorption band at 1306 cm⁻¹. The IR spectrum of methyl acetate shows a strong absorption from the C=O stretching vibration over the interval 1740–1800 cm⁻¹ which was used to determine the concentrations.

The expected ratio of k_4 and k_3 (Using the rate constants given in Table 1) is $k_4/k_3 = 0.049(\pm 0.006)$.

From the experiment done with only the two references present, the following relative rate was obtained: $k_4/k_3 = 0.049$ (±0.002). The relative rate plots for the chlorine reaction of methyl acetate are shown in Fig. 1a. The following relative rates were obtained: $k_1/k_3 = 0.249(\pm 0.013)$, $k_1/k_4 = 3.931(\pm 0.158)$.

From the two relative rate expressions the average rate constant of the reaction is

$$k_1 = (1.93 \pm 0.27) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$



Fig. 1b. Relative rate plots for the OH-reaction of methyl acetate at 293(±0.5) K and a total air pressure of 980 mbar.

The quoted error corresponds to two standard deviations and is computed as the root mean square of the errors on the two rate constants obtained relative to k_3 and k_4 . The results are summarized in Table 2. The rate constant is in good agreement with the rate obtained by Christensen et al. [12]. However, it does not agree with the rate constants determined by Notario et al. and Cuevas et al. [17,18] (see Table 2).

We note that the rate constant determined using C_2H_5Cl is in good agreement with previous work. The rate constant determined using CH₃Br as a reference is lower than the other rates (see Table 2). However, the ratio of k_4/k_3 is in excellent agreement with the literature. We therefore suggest that the rate of reaction of methyl acetate with atomic chlorine may be lower than presented by Notario et al. and Cuevas et al. [17,18].

4.2. OH-experiments

For the reaction of methyl acetate with OH, CH_2FCH_2F and C_2H_6 were used as reference compounds. The absorption peaks from the C–H stretching vibrations at 2895 and 2995 cm⁻¹ were used to determine the concentrations of C_2H_6 and CH_2FCH_2F , respectively. The expected ratio of k_6 and k_5 (Using the rate constants given

in Table 1) is $k_6/k_5 = 2.585(\pm 1.091)$.

Table 2

Results for the reactions of methyl acetate with Cl and OH obtained in this study and in earlier studies.

Reaction	$k \times 10^{12} \mathrm{cm^3} \mathrm{molecule^{-1}} \mathrm{s^{-1}}$	Ref.
(1) $CH_3C(O)OCH_3 + Cl \rightarrow products$	(2.17 ± 0.23)	This study (relative to k_3)
(1) $CH_3C(O)OCH_3 + Cl \rightarrow products$	(1.69 ± 0.14)	This study (relative to k_4)
(1) $CH_3C(0)OCH_3 + Cl \rightarrow products$	(1.93 ± 0.27)	This study
(1) $CH_3C(0)OCH_3 + Cl \rightarrow products$	(2.85 ± 0.35)	[17]
(1) $CH_3C(0)OCH_3 + Cl \rightarrow products$	(2.2 ± 0.3)	[12]
(1) $CH_3C(0)OCH_3 + Cl \rightarrow products$	(2.73 ± 0.30)	[18]
(2) $CH_3C(0)OCH_3 + OH \rightarrow products$	(0.322 ± 0.003)	This study (relative to k_5)*
(2) $CH_3C(0)OCH_3 + OH \rightarrow products$	(0.315 ± 0.013)	This study (relative to k_6)
(2) $CH_3C(0)OCH_3 + OH \rightarrow products$	(0.318 ± 0.013)	This study
(2) $CH_3C(0)OCH_3 + OH \rightarrow products$	(0.341 ± 0.029)	[19]
(2) $CH_3C(0)OCH_3 + OH \rightarrow products$	(0.342 ± 0.009)	[20]
(2) $CH_3C(0)OCH_3 + OH \rightarrow products$	(0.385 ± 0.015)	[21]
(2) $CH_3C(0)OCH_3 + OH \rightarrow products$	(0.170 ± 0.050)	[22]

* Error derived using the standard error of the relative rate plot (two sigma) and does not include systematic error or the error in the rate of k5.



Fig. 2. The proposed mechanism for the OH initiated oxidation of methyl acetate [12,13].

From the experiment done with only the two references present, the following relative rate was obtained: $k_6/k_5 = 2.615(\pm 0.059)$

Together with the experiments done with the two reference reactions for the chlorine reaction these experiments demonstrate the reliability of the experimental system.

The relative rate plots from the reaction of methyl acetate with OH shown in Fig. 1b were used to determine the following relative rates: $k_2/k_5 = 3.667 \pm 0.015$, $k_2/k_6 = 1.385 \pm 0.029$.

From the two relative rate expressions the average rate constant of the reaction is

$$k_2 = (3.18 \pm 0.13) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The quoted error corresponds to two standard deviations.

The results obtained using the two reference compounds agree with each other to within the uncertainty limits. All results including those from previous studies are summarized in Table 2.

The rate constant determined for reaction (2) is in good agreement with the rate constants determined by Wallington et al., El Boudali et al., and Smith et al. [19–21] for this reaction (see Table 2). The rate constant determined by Campbell and Parkinson is significantly lower than the rate constants determined in all other studies including the one determined in the present study [22].

5. Results for the product studies

The reaction of methyl acetate with Cl was studied in the presence and absence of oxygen and NO. The following four experiments were performed:

- (1) Methyl acetate + Cl in 980 mbar N₂.
- (2) Methyl acetate + Cl in 980 mbar air.
- (3) Methyl acetate + Cl in 980 mbar air, containing NO.
- (4) Methyl acetate + Cl in 980 mbar O_2 , containing NO.

The possible OH initiated breakdown mechanism for methyl acetate is illustrated in Fig. 2. As mentioned, Cl-initiated oxidation is expected to proceed via a similar mechanism.

The reaction with Cl proceeds via hydrogen abstraction from one of the C–H bonds in the molecule, leading to either of the two radicals generated by reactions (7) and (8):

$$CH_{3}C(0)OCH_{3} + Cl \rightarrow CH_{3}C(0)OCH_{2} + HCl$$

$$CH_{3}C(0)OCH_{3} + Cl \rightarrow CH_{2}C(0)OCH_{3} + HCl$$
(8)

H-abstraction from the alkoxy-end has been observed to be the more probable of the two reactions [12,13]. This was confirmed by the present study. In the absence of oxygen two products were observed, one being primary and the other secondary. Spectra of both compounds are shown in Fig. 3. Comparison with calibrated reference spectra recorded at the same conditions as for the reactants showed that the two products could not be attributed to dimethyl succinate $(CH_2O(O)C(CH_2)_2C(O)OCH_3)$, ethylene glycol, diacetate $(CH_3C(O)O(CH_2)_2O(O)CCH_3)$ or chloro acetic acid $(ClCH_2C(O)OCH_3)$. The most likely explanation is, therefore, that the primary product is $CH_3C(O)OCH_2Cl$ formed by reaction (9), and the secondary product is $CH_3C(O)OCH(Cl)_2$ formed from the primary product by reaction (10) and (11) [12,13].

$$\begin{array}{ll} CH_3C(0)OCH_2^{\cdot}+Cl_2\rightarrow CH_3C(0)OCH_2Cl+Cl^{\cdot} & (9) \\ CH_3C(0)OCH_2Cl+Cl^{\cdot}\rightarrow CH_3C(0)OCH(\cdot)Cl+HCl & (10) \end{array}$$

$$CH_{3}C(0)OCH(\cdot)Cl + Cl_{2} \rightarrow CH_{3}C(0)OCH(Cl)_{2}$$
(11)

The IR spectra of the proposed primary product $CH_3C(O)OCH_2Cl$ and the secondary product $CH_3C(O)OCHCl_2$ were calculated at the B3LYP/6-31+G(d) level of theory for *cis* and *trans* optimised geometries of the chlorinated group relative to the carbonyl group. The calculations showed that the carbonyl vibration of the secondary product will shift to higher frequency and have a reduced intensity relative to the primary product. This calculation, at a rather basic level of theory, fits the experimental observation very well and further supports our assignment. The calculated spectra are available as electronic supplementary material. In addition to these two species there are other Cl-substituted analogues of $CH_3C(O)OCH_3$ that will contribute to the measured peaks.

The peak from the primary product has a shoulder that is preserved, but decreases, as the secondary product is formed. A possible explanation is the formation of another primary product, $CICH_2C(O)OCH_3$ according to reaction (12). Comparison with a calibrated spectrum of this compound did not however confirm its presence. The shoulder is therefore most likely due to other chlorinated compounds.

$$CH_3C(0)OCH_2^{\cdot} + Cl_2 \rightarrow CICH_2C(0)OCH_3 + CI^{\cdot}$$
(12)

Apart from $CH_3C(O)OCH(Cl)_2$, formation of other secondary products such as $ClCH_2C(O)OCH_2Cl$ and $(Cl)_2C(O)OCH_3$ is possible by reactions similar to reactions (10) and (11). A shoulder seen on the secondary product peaks could be due to either of these compounds.

In the presence of oxygen, peroxy radicals will be formed by addition of O_2 to the radicals formed by reaction (7) and (8), illustrated in reaction (13) for the radical generated by reaction (7):

$$CH_3C(0)OCH_2^{-} + O_2 \rightarrow CH_3C(0)OCH_2OO^{-}$$
 (13)

These peroxy radicals can either rearrange to form anhydrides and hydroxyl compounds (reaction (14)), or they can form alkoxy radicals by self reaction (reaction (15)) or by reaction with NO (reaction (16)) [12,13].



Fig. 3. Spectra obtained for the reaction of methyl acetate with Cl in 980 mbar N_2 at 293 K. The first spectrum was obtained before UV-irradiation. The second spectrum was obtained after 34 s of irradiation and shows the primary product. The last spectrum was obtained after 17.5 min irradiation and shows the secondary product.

$$2CH_3C(0)OCH_2OO \rightarrow CH_3C(0)OCHO + CH_3C(0)OCH_2OH$$
(14)

$$2CH_3C(0)OCH_2OO^{\cdot} \to 2CH_3C(0)OCH_2O^{\cdot} + O_2$$
(15)

$$CH_3C(0)OCH_2OO^{\circ} + NO \rightarrow CH_3C(0)OCH_2O^{\circ} + NO_2$$
(16)

The alkoxy radicals formed by reaction (15) and (16) can either rearrange to form acetic acid (CH₃C(O)OH) and the formyl radical (.CHO) (reaction (17)), or they can react with O_2 to form acetic formic anhydride (CH₃C(O)OCHO) (reaction (18)).

$$CH_3C(0)OCH_2O \rightarrow CH_3C(0)OH + CHO$$
(17)

$$CH_3C(0)OCH_2O' + O_2 \rightarrow CH_3C(0)OCHO + HO_2'$$
(18)

The only products observed in the reaction of methyl acetate with Cl in 980 mbar air and in the absence of NO were acetic formic anhydride, CO, and CO₂, which excludes reaction (14). The formation of acetic formic anhydride very likely arises from the oxy radicals formed in reaction (15), and the formation of the product was observed to correlate linearly with the decrease in methyl acetate concentration (see Fig. 4). The formation of acetic formic anhydride and CO account for $85.5 \pm 9.2\%$ of the loss of methyl acetate. The molar yield of CO was 23.2 ± 3.3%. Since three CO molecules can be formed from one methyl acetate molecule, this accounts for $7.7 \pm 1.1\%$ of the total methyl acetate loss. The 77.8 ± 9.3% yield of acetic formic anhydride is in agreement to within experimental error with the results from Christensen et al., $66 \pm 7\%$ [12]. The quoted errors correspond to two standard deviations. Wall reactions creating CO may also be present but their contribution could not be quantified in the present work. The experiment shows that hydrogen abstraction occurs primarily from the alkoxy end of the molecule, supporting the assumption that the primary product formed in the absence of oxygen is CH₃C(O)OCH₂Cl.

In the presence of NO, formic acid, acetic acid and formaldehyde were produced as well as acetic formic anhydride, CO and CO₂. Acetic acid can be formed via the α -ester rearrangement from alkoxy radicals generated by either reaction (15) or (16). Since the compound was only formed in the presence of NO, it is concluded that it is formed by the alkoxy radicals generated via reaction (16). In the studies done by Christensen et al. and Tyndall et al. acetic acid was generated to a higher extent when NO was present, confirming the assumption that oxy radicals generated by reaction with NO are more likely to undergo α -ester rearrangement than oxy radicals generated by the self reaction (15) [12,13]. Christensen et al. explained this phenomenon by the formation of excited alkoxy radicals on reaction with NO (reaction (16)). These excited radicals would have enough energy to overcome the exothermic barrier for the α -ester rearrangement [12]. Acetic acid was not observed in the absence of NO in the present study. The acetic acid yield in the study by Christensen et al. was 11 ± 3%. An estimate of the lower limit for detection of CH₃COOH in our system corresponds to 0.05 ppm or a yield of ca. 0.5%. Tyndall et al. used Cl₂ initial concentrations that were 2-3 times higher and NO concentrations that were 2 times higher than the initial concentrations of methyl acetate whereas Christensen et al. used initial Cl₂ concentrations that were 1-25 times the concentration of methyl acetate, and NO initial concentrations that were equal to or half of the concentrations of methyl acetate [12,13]. Initial concentrations of methyl acetate in the two experiments were similar to the ones used in the present study. Thus, the observed differences were not caused by differences in the concentrations of reactants used in the different studies.

A few percent of formaldehyde were formed, either through hydrolysis of acetic formic anhydride or reactions involving formaldehyde produced by the decomposition of alkoxy radicals according to (19) [12].

$$CH_3C(0)OCH_2O' \rightarrow CH'_3 + CO_2 + HCHO$$
(19)

Formaldehyde can be converted to formic acid by processes involving the walls, OH, HO_2 or RO_2 , but note that HO_2 will be suppressed in the presence of NO [23].

In 980 mbar oxygen with NO, the same products were observed as in 980 mbar air with NO. In both experiments loss of methyl acetate was observed to correlate linearly with the formation of acetic formic anhydride, acetic acid, and formic acid (shown in Fig. 4). Molar yields of acetic acid in the two experiments were $36.8 \pm 3.0\%$ and $38.0 \pm 3.0\%$, respectively. The molar yields of acetic formic anhydride in the two experiments were $42.8 \pm 4.0\%$ and $50.0 \pm 6.0\%$, respectively, while those for formic acid were $3.7 \pm 0.7\%$ and $6.0 \pm 1.0\%$, respectively. Quoted errors

correspond to two standard deviations. Branching ratios for the formation of acetic formic anhydride and acetic acid were not significantly different for the two experiments, and therefore it can be concluded that there is no oxygen dependence of the α -ester rearrangement in the pressure range used in the present experiments.

The formation of the mentioned products account for $78.9 \pm 7.4\%$ of the total loss of methyl acetate. Apart from the observed products, unknown primary products that absorb at 1250, 1350, 1675 and 1700 cm⁻¹, and secondary products that absorb at 1050 and 1850 were observed. The absorption peaks at 1350 and 1675 cm⁻¹ are most likely to be due to N-O stretching vibrations. The intensity of these peaks were observed to increase as



Fig. 4. Correlations between the formation of products formed and methyl acetate loss for the reaction in 980 mbar air in the absence (left) and presence (right) of NO.



Fig. 5. Residual spectra of the reaction of methyl acetate with Cl in 980 mbar air containing NO, after subtraction of all known products. The first spectrum was recorded after 5 min of irradiation, and the last spectrum was recorded after irradiation of 1 h and 10 min. Peaks attributed to the formation of NOCI and NO₂ are indicated.

the peak from NO₂ decreased. This is illustrated in the residual spectra in Fig. 5. One of the primary products could be $CH_3C(0)O$ -CH₂ONO₂ formed from addition of NO to peroxyl radicals [12]. The yield of acetic acid and acetic formic anhydride in the experiments performed in the presence of NO do not change over the range of O2 concentrations used (206 to 980 mbar), which is consistent with the work of Christensen et al. [12].

6. Implications for atmospheric chemistry

The degradation of methyl esters in the atmosphere is primarily initiated by hydroxyl radicals because of the combination of high reactivity with the concentration of this radical. Reaction with NO₃ as well as photolytic breakdown are additional possible removal processes for methyl acetate. These processes have been studied by Langer et al. and Benayada et al., and both were found to be negligible compared to reaction with OH [24,25]. Atmospheric lifetimes of the esters can, therefore, be determined from their reaction rates with the hydroxyl radical. From the rate constants determined in this study and an OH concentration of 1×10^6 molecule cm⁻³, the following lifetime is expected for methyl acetate:

τ (CH₃C(O)OCH₃ + OH) = 29-46 days

The relatively long lifetime and the fact that esters have low solubility in the aqueous phase [12,26] imply that long distance transport of methyl acetate will be significant.

In the marine boundary layer where reactions with atomic chlorine can be important, the expected lifetime for methyl acetate at peak chlorine concentrations of 10⁶ radicals cm⁻³ is:

$(CH_3C(0)OCH_3 + Cl) = 4.5 - 9$ days

Since this is based on a maximum Cl concentration, removal by Cl is contingent on specific local circumstances. The fate of formaldehyde formed by the oxidation of methyl acetate includes photolysis and reaction with OH, Cl, or other radicals.

The acids formed react slowly with oxidants in the atmosphere. Hence, the most likely fate of these is wet or dry deposition or long distance transport. In the atmosphere acetic formic anhydride will react rapidly with water to form formic and acetic acid [27].

Methyl acetate reacts slowly with OH radicals, making atmospheric impact by products possible far from the emission source. Reactivity with OH radicals increases with increasing chain length of the ester because of the presence of a greater number of hydrogens. For longer chained methyl esters, reaction is expected to be increasingly faster making long distance transport less important. Products for longer chained saturated methyl esters are expected to resemble the products observed in the present study. The present study serves as a model for product branching ratios for longer chained methyl esters.

Acknowledgements

The authors thank the Copenhagen Center for Atmospheric Research, sponsored by the Danish Natural Science Research Council and the Villum Kann Rasmussen Fund, for its generous support. Furthermore, we thank Dr. Timothy Wallington and the reviewers for helpful advice.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cplett.2009.02.066.

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