Atmospheric Oxidation Mechanism of Methyl Propionate

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Smog chamber FTIR techniques were used to study the atmospheric oxidation of methyl propionate in 740 Torr of air in the presence of NO_x at 296 ± 2K. Relative rate techniques were used to measure $k(OH + CH_3CH_2C(O)OCH_3) = (9.29 \pm 1.13) \times 10^{-13}$, $k(Cl + CH_3CH_2C(O)OCH_3) = (1.51 \pm 0.22) \times 10^{-11}$, $k(Cl + CH_3CH_2C(O)OC(O)H) = (2.89 \pm 0.35) \times 10^{-12}$, $k(Cl + CH_3CH_2C(O)OH) = (4.72 \pm 0.62) \times 10^{-12}$, and $k(Cl + CH_3C(O)C(O)OCH_3) = (4.99 \pm 0.96) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The products (and molar yields) formed in the Cl-atom initiated oxidation of methyl propionate were as follows: propionic formic anhydride ($CH_3CH_2C(O)OC(O)H$), 0.099 ± 0.019; propionic acid ($CH_3CH_2C(O)OH$), 0.139 ± 0.027; carbon monoxide, 0.132 ± 0.026; methyl pyruvate ($CH_3C(O)C(O)OCH_3$), 0.289 ± 0.057; acetaldehyde, 0.077 ± 0.015; methoxy formylperoxynitrate ($CH_3OC(O)O_2NO_2$), 0.083 ± 0.016; methyl glyoxylate ($H(O)CC(O)OCH_3$), 0.111 ± 0.022; organic nitrates, 0.07 ± 0.02; and formaldehyde. These products account for 79 ± 16% of the loss of methyl propionate. The atmospheric oxidation mechanism of methyl propionate is presented and discussed.

1. Introduction

Esters are used as industrial solvents and as reagents during the manufacture of perfumes and food flavoring. Esters are also emitted into the atmosphere from natural sources (i.e., vegetation) and are formed in the atmosphere as oxidation products of ethers used as automotive fuel additives.[1−3] Prompted by the need for more environmentally compatible solvents (i.e., compounds which will reduce the level of photooxidant formation in the troposphere), there is commercial interest in the use of esters such as methyl propionate as replacements for traditional solvents. Esters are volatile organic compounds and may be released into the atmosphere during their use (methyl propionate has a boiling point of 79 °C). Increased use of esters as solvents will lead to increased emissions into the atmosphere. Assessment of the contribution of esters to the formation of ozone and other photooxidants in urban air masses requires detailed kinetic and mechanistic information concerning their atmospheric oxidation.

Despite its importance, the atmospheric oxidation mechanism of esters has received relatively little attention. To improve our understanding of the atmospheric chemistry of esters, and to facilitate an accurate description of such in atmospheric models, we have conducted a study of the atmospheric oxidation products of methyl propionate. The atmospheric oxidation is initiated by reaction with OH radicals.

$$CH_3CH_2C(O)OCH_3 + OH \rightarrow CH_3CH_2C(O)OCH_2\cdot + H_2O$$

$$CH_3CH_2C(O)OCH_3 + OH \rightarrow CH_3CH(\cdot)C(O)OCH_3 + H_2O$$

$$CH_3CH_2C(O)OCH_3 + OH \rightarrow \cdot CH_2CH_2C(O)OCH_3 + H_2O$$

Under atmospheric conditions the alkyl radicals above react with oxygen to give peroxy radicals.

$$CH_3CH_2C(O)OCH_2\cdot + O_2 + M \rightarrow CH_3CH_2C(O)OCH_2O_2\cdot + M$$

$$CH_3CH(\cdot)C(O)OCH_3 + O_2 + M \rightarrow CH_3CHOO(\cdot)C(O)OCH_3 + M$$

$$\cdot CH_2CH_2C(O)OCH_3 + O_2 + M \rightarrow \cdot OOCH_2CH_2C(O)OCH_3 + M$$

Peroxy radicals react with NO, NO_2, HO_2, and other peroxy radicals in the atmosphere.[4,5] Reaction with NO dominates in polluted air masses and proceeds via two channels giving alkoxy radicals as major and organic nitrates as minor products. In this work we have studied the fate of the three different alkoxy radicals formed in the atmospheric oxidation of methyl propionate: $CH_3CH_2C(O)OCH_2O\cdot$, $CH_3CHO(\cdot)C(O)OCH_3$, and $\cdot OCH_2CH_2C(O)OCH_3$. The alkoxy radicals were prepared by UV irradiation of methyl propionate/Cl_2/NO_x mixtures in 740 Torr of air at 296 K. As part of this work, the kinetics of the reactions of OH radicals and Cl atoms with methyl propionate and Cl atoms with the oxidation products of methyl propionate were determined.

2. Experimental Section

All experiments were carried out in a 405 L Pyrex cylindrical glass reactor with Teflon coated metal end flanges described in detail elsewhere.[6] A White mirror system mounted inside the reactor and coupled with an external mirror system to a Fourier transform-spectrometer (Nicolet Magna 550) enables in situ monitoring of both reactants and products by long path infrared

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absorption (total path length 50.4 m). The reactor is equipped with 18 fluorescent lamps (Philips TLA 40W/05, $300 \leq \lambda \leq 450$ nm; $\lambda_{max} = 365$ nm) arranged concentrically around the outside of the chamber and with three low-pressure mercury vapor lamps (Philips TUV 40W; $\lambda_{max} = 254$ nm) contained inside a quartz glass tube mounted centrally inside the chamber between the end flanges; both lamp types were employed for the photolysis experiments.

The oxidation of methyl propionate, $CH_3CH_2C(O)OCH_3$, was initiated by reaction with Cl atoms, generated by photolysis of molecular chlorine, in 740 Torr synthetic air at 296 ± 2 K. To test for heterogeneous and/or photolytic losses of methyl propionate and its oxidation products, two control experiments were performed. First, methyl propionate/air mixtures were left to stand in the dark in the chamber for 15 min and then subjected to UV irradiation for 15 min. There was no observable loss (<3%) of methyl propionate. Second, product mixtures obtained following UV irradiation of methyl propionate/Cl_2/NO_x/air mixtures were left to stand in the chamber in the dark for 15 min. There was no observable loss (<3%) of any products. Calibration of methyl propionate ($CH_3CH_2C(O)OCH_3$), propionic formic anhydride ($CH_3CH_2C(O)OC(O)H$), propionic acid ($CH_3CH_2C(O)OH$), and methyl pyruvate ($CH_3C(O)C(O)OCH_3$) was achieved by injecting known amounts of these compounds into the evacuated chamber in a heated gas stream. Methyl glyoxalate is not available commercially. An infrared spectrum of methyl glyoxylate, $H(O)CC(O)OCH_3$, was obtained by photolysis of methyl bromoacetate at 254 nm in the presence of NO in 740 Torr of air.

$$BrCH_2C(O)OCH_3 + h\nu + O_2 \rightarrow Br + {\cdot}O_2CH_2C(O)OCH_3$$

$${\cdot}O_2CH_2C(O)OCH_3 + NO \rightarrow {\cdot}OCH_2C(O)OCH_3 + NO_2$$

$${\cdot}OCH_2C(O)OCH_3 + O_2 \rightarrow H(O)CC(O)OCH_3 + HO_2$$

Photolysis of $BrCH_2C(O)OCH_3$ gives the ${\cdot}CH_2C(O)OCH_3$ radical which, after addition of O_2 and reaction with NO, leads to the ${\cdot}OCH_2C(O)OCH_3$ alkoxy radical. There are three possible fates for the ${\cdot}OCH_2C(O)OCH_3$ radical: reaction with O_2 to give methyl glyoxylate, elimination of HCHO to give a ${\cdot}C(O)OCH_3$ radical, or isomerization to give $HOCH_2C(O)OCHO$ and/or $HC(O)C(O)OCH_2OH$. The major fate of ${\cdot}OCH_2C(O)OCH_3$ was reaction with O_2 to give methyl glyoxylate which was identified by virtue of its IR features 2966, 2850, 1754, 1741, 1289, 1225, and 1024 cm^{-1}. Decomposition via elimination of HCHO accounted for 4% of the loss of the ${\cdot}OCH_2C(O)OCH_3$ alkoxy radical. The lack of any distinctive OH stretching vibrational features in the residual spectra at ~3670 cm^{-1} showed that isomerization to $HOCH_2C(O)OCHO$ and/or $HC(O)C(O)OCH_2OH$ is of little or no importance. The methyl glyoxylate spectrum was calibrated by assuming a 96% photolytic conversion of methyl bromoacetate into methyl glyoxylate.

For completeness, experiments were performed in which ozone was added to methyl crotonate ($CH_3\text{-}CH{=}CHC(O)OCH_3$)/air mixtures. The ozonolysis of methyl crotonate is expected to produce methyl glyoxalate plus acetaldehyde in unit yields.[7] The methyl glyoxylate spectrum was calibrated in this case assuming its yield was equal to the measured concentration of acetaldehyde. The infrared absorption cross sections obtained for methyl glyoxalate from these experiments were within ±10% of those obtained from the photolysis of methyl bromoacetate, thus giving added confidence in the calibration of the methyl glyoxylate reference spectrum.

Quantitative reference spectra of formaldehyde, acetaldehyde, acetylperoxynitrate, methoxy formylperoxynitrate, and carbon monoxide were taken from the infrared library at Wuppertal.

Chemicals. Propionic formic anhydride $CH_3CH_2C(O)OC(O)H$ was synthesized following a procedure similar to that described for acetic formic anhydride.[8] Briefly, propionyl chloride (Aldrich, 97%) was added to finely ground sodium formate (Fluka, 99.5%) while the temperature was maintained at 23−27 °C using a cooling bath. The mixture was then filtered with suction and the solid residue rinsed with diethyl ether. After removal of the ether, the filtrate was distilled under reduced pressure to yield propionic formic anhydride as a colorless liquid. Methyl propionate (>99% GC), propionic acid (>99%), methyl pyruvate (>98%), 2-Br-methyl acetate (>97%), and methyl formate (>99%) were purchased from Aldrich; Cl_2 (>99.8%), NO (>99.95%), chloroethane (>99%), ethane (99.95%), chloromethane (>99.8%), and synthetic air were supplied by Messer Griesheim.

3. Results and Discussion

3.1. Relative Rate Studies of *k*(Cl + Methyl Propionate), *k*(Cl + Propionic Formic Anhydride), *k*(Cl + Propionic Acid), and *k*(Cl + Methyl Pyruvate).

Prior to investigating the atmospheric oxidation products of $CH_3CH_2C(O)OCH_3$, relative rate experiments, as described in Atkinson,[9] were performed in 740 Torr of synthetic air at 296 ± 2 K to determine the kinetics of reaction 1, 2, 3, and 4.

$$Cl + CH_3CH_2C(O)OCH_3 \rightarrow \text{products} \quad (1)$$

$$Cl + CH_3CH_2C(O)OC(O)H \rightarrow \text{products} \quad (2)$$

$$Cl + CH_3CH_2C(O)OH \rightarrow \text{products} \quad (3)$$

$$Cl + CH_3C(O)C(O)OCH_3 \rightarrow \text{products} \quad (4)$$

Initial concentrations used were $CH_3CH_2C(O)OCH_3$, $(2-3) \times 10^{14}$; $CH_3CH_2C(O)OC(O)H$, $(1-3) \times 10^{14}$; $CH_3CH_2C(O)OH$, $(3-4) \times 10^{14}$; $CH_3C(O)C(O)OCH_3$, 3×10^{14}; C_2H_5Cl, $(4-5) \times 10^{14}$; C_2H_6, $(5-7) \times 10^{14}$; $CH_3OC(O)H$, $(5-12) \times 10^{13}$; CH_3Cl, $(5-10) \times 10^{14}$; and Cl_2, $(6-30) \times 10^{14}$ molecule cm^{-3}. Reaction 1 was measured relative to reactions 5 and 6. Reaction 2 was measured relative to reactions 5 and 7. Reaction 3 was measured relative to reactions 5 and 7. Reaction 4 was measured relative to reactions 7 and 8.

$$Cl + C_2H_5Cl \rightarrow \text{products} \quad (5)$$

$$Cl + C_2H_6 \rightarrow \text{products} \quad (6)$$

$$Cl + CH_3OC(O)H \rightarrow \text{products} \quad (7)$$

$$Cl + CH_3Cl \rightarrow \text{products} \quad (8)$$

Figures 1−4 show plots of the losses of $CH_3CH_2C(O)OCH_3$, $CH_3CH_2C(O)OC(O)H$, $CH_3CH_2C(O)OH$, and $CH_3C(O)C(O)OCH_3$ versus those of the reference compounds following exposure to Cl atoms. Rate constant ratios derived from linear least squares analyses of the data in Figures 1−4 are given in Table 1. The rate constant ratios can be placed on an absolute basis using $k_5 = 8.04 \times 10^{-12}$,[10] $k_6 = 5.7 \times 10^{-11}$,[11] $k_7 = 1.4 \times 10^{-12}$,[12] and $k_8 = 4.8 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}.[13] The resulting absolute values of k_1, k_2, k_3, and k_4 are listed in Table 1. Uncertainties quoted for k_1, k_2, k_3, and k_4 in Table 1 include statistical uncertainties (2 standard deviations) from analyses

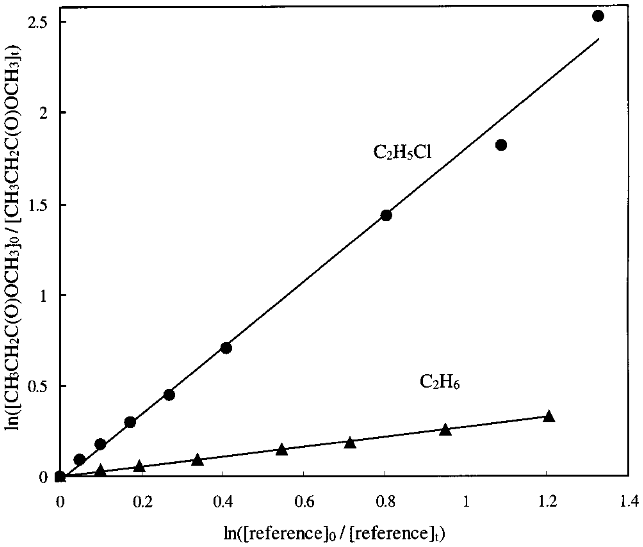


Figure 1. Loss of methyl propionate versus C_2H_5Cl (circles) and C_2H_6 (triangles) following exposure to Cl atoms in 740 Torr synthetic air at 296 K.

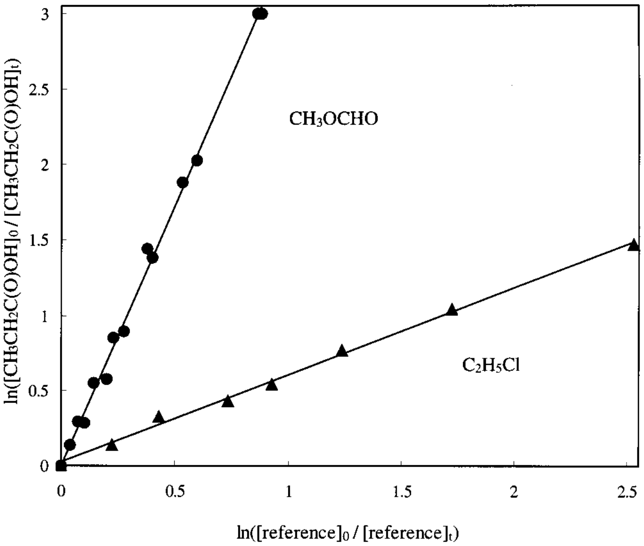


Figure 2. Loss of propionic acid versus methyl formate (circles) and C_2H_5Cl (triangles) following exposure to Cl atoms in 740 Torr synthetic air at 296 K.

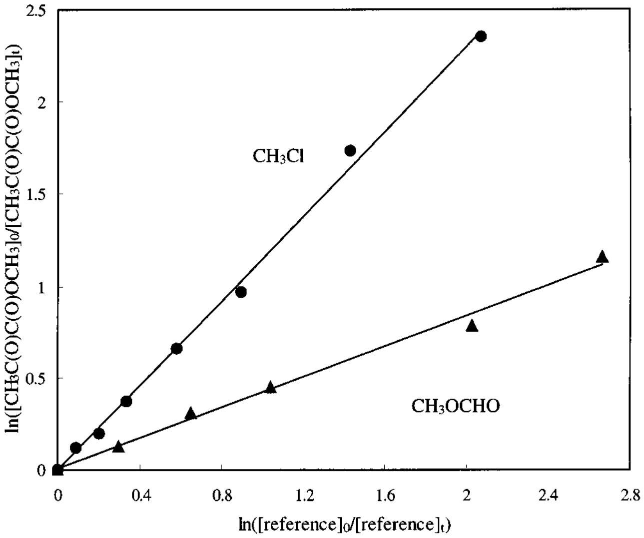


Figure 3. Loss of methyl pyruvate versus CH_3Cl (circles) and methyl formate (triangles) following exposure to Cl atoms in 740 Torr synthetic air at 296 K.

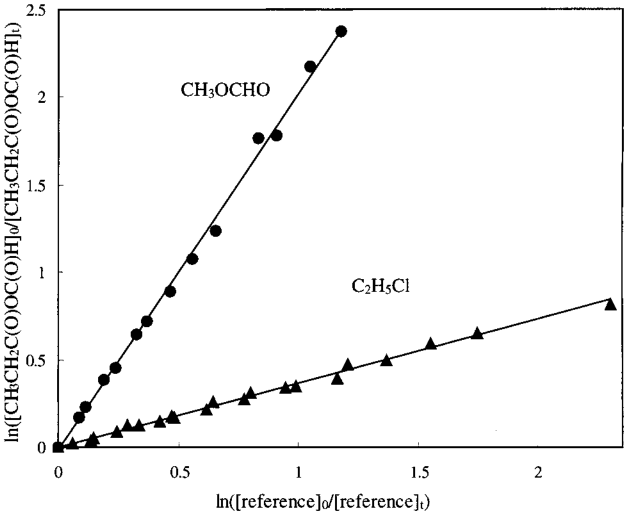


Figure 4. Loss of propionic formic anhydride versus methyl formate (circles) and C_2H_5Cl (triangles) following exposure to Cl atoms in 740 Torr synthetic air at 296 K.

of the data in Figures 1−4 and an additional 10% uncertainty to account for uncertainties in the reference rate coefficients. As seen from Table 1, indistinguishable results were obtained from experiments using different reference compounds. We choose to cite final values of k_1, k_2, k_3, and k_4 which are averages of the individual determinations together with error limits which encompass the extremes of the individual determinations. Hence, $k_1 = (1.51 \pm 0.22) \times 10^{-11}$; $k_2 = (2.89 \pm 0.35) \times 10^{-12}$; $k_3 = (4.72 \pm 0.62) \times 10^{-12}$; and $k_4 = (5.73 \pm 0.96) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. We are the first to study k_2, k_3, and k_4 and so cannot compare our results with previous determinations.

The value of k_1 determined in this study is 24% lower than that of $k_1 = 1.98 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} reported by Notario et al.[14] from a study of the reaction of Cl atoms with a series of esters. Interestingly, Christensen et al.[15] measured a value for k(Cl + methyl acetate) which was 23% lower than that reported by Notario et al.,[14] Langer et al.[16] measured a value of k(Cl + *tert*-butyl acetate) which was 34% lower than that reported by Notario et al.,[14] and Wallington et al.[12] measured a value of k(Cl + methyl formate) which was 23% lower than that reported by Notario et al.[14] It appears that Notario et al.[14] have systematically overestimated the reactivity of Cl atoms toward esters.

3.2. Relative Rate Study of *k*(OH + Methyl Propionate). The kinetics of reaction 9 in 740 Torr of air at 295 K were measured relative to reactions 10 and 11.

$$CH_3CH_2C(O)OCH_3 + OH \rightarrow \text{products} \tag{9}$$

$$CH_3OH + OH \rightarrow \text{products} \tag{10}$$

$$C_2H_5OH + OH \rightarrow \text{products} \tag{11}$$

Initial concentrations were methyl propionate, (2−3) × 10^{14}; CH_3ONO, (0.5−1) × 10^{14}; NO, (4−5) × 10^{14} molecule cm^{-3}; and CH_3OH, (4−6) × 10^{14}; or C_2H_5OH, (3−4) × 10^{14} in 740 Torr of air diluent. The observed loss of methyl propionate versus those of reference compounds in the presence of OH radicals is shown in Figure 5. Linear least-squares analysis of the data gives $k_9/k_{10} = 1.01 \pm 0.04$ and $k_9/k_{11} = 0.28 \pm 0.01$. Using $k_{10} = 9.32 \times 10^{-13}$ and $k_{11} = 3.27 \times 10^{-12}$ cm^3

TABLE 1: Kinetic Data for Reactions of Cl Atoms with Methyl Propionate, Propionic Formic Anhydride, Propionic Acid, and Methyl Pyruvate, Measured at 296 ± 2 K

	$CH_3CH_2C(O)OCH_3$		$CH_3CH_2C(O)OC(O)H$		$CH_3CH_2C(O)OH$		$CH_3C(O)C(O)OCH_3$	
reference	$k_1/k_{reference}$[a]	k_1[b]	$k_2/k_{reference}$[a]	k_2[b]	$k_3/k_{reference}$[a]	k_3[b]	$k_4/k_{reference}$[a]	k_4[b]
C_2H_5Cl	1.77 ± 0.02	$(1.49 \pm 0.15) \times 10^{-11}$	0.36 ± 0.01	$(2.94 \pm 0.31) \times 10^{-12}$	0.58 ± 0.03	$(4.66 \pm 0.53) \times 10^{-12}$		
C_2H_6	0.27 ± 0.02	$(1.54 \pm 0.19) \times 10^{-11}$						
$CH_3OC(O)H$			2.04 ± 0.07	$(2.85 \pm 0.31) \times 10^{-12}$	3.42 ± 0.20	$(4.79 \pm 0.55) \times 10^{-12}$	0.42 ± 0.04	$(5.88 \pm 0.81) \times 10^{-13}$
CH_3Cl							1.16 ± 0.12	$(5.57 \pm 0.80) \times 10^{-13}$

[a] The indicated error for the rate constant ratios is 2σ. [b] The rate constants are given in units of cm^3 $molecule^{-1}$ s^{-1}.

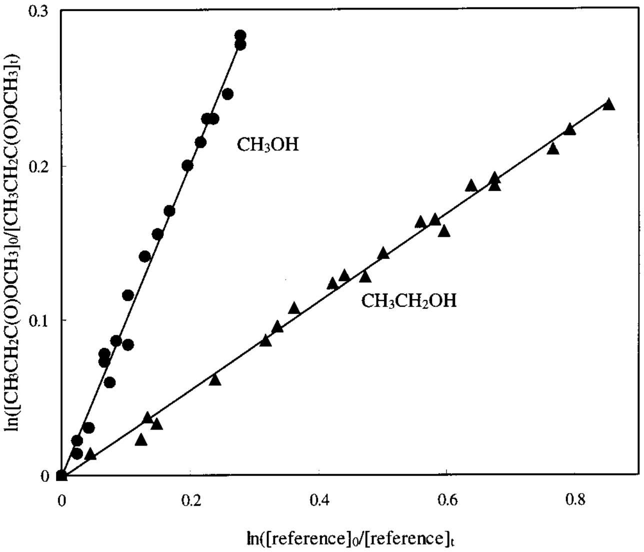


Figure 5. Loss of methyl propionate versus methanol (circles) and ethanol (triangles) following exposure to OH radicals in 740 Torr synthetic air at 296 K.

molecule^{-1} s^{-1}[1],[7] we derive $k_9 = (9.41 \pm 0.37) \times 10^{-13}$ and $(9.16 \pm 0.33) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. We estimate that potential systematic errors associated with uncertainties in the reference rate constants add a 10% uncertainty range for k_9. Propagating this additional uncertainty gives $k_9 = (9.41 \pm 1.01) \times 10^{-13}$ and $(9.16 \pm 0.97) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. We choose to cite a final value for k_9 which is the average of those determined using the two different reference compounds together with error limits which encompass the extremes of the individual determinations. Hence, $k_9 = (9.29 \pm 1.13) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. Quoted error reflects the accuracy of the measurements. This result is in excellent agreement with the absolute rate constants $k_9 = (10.3 \pm 0.4) \times 10^{-13}$ and $k_9 = (8.31 \pm 0.87) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1} reported previously by Wallington et al.[18] and by Le Calvé et al.,[19] respectively. In light of the agreement between the three studies we recommend use of the average of the three determinations, $k_9 = 9.3 \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}, in models of the atmospheric chemistry of methyl propionate.

It is interesting at this stage to compare the relative reactivities of Cl and OH with respect to reaction with methyl propionate. The rate coefficient for reaction of OH with $CH_3CH_2C(O)OCH_3$ is quite close to that for the reaction of OH with $CH_3CH_2CH_3$, $k(OH + CH_3CH_2CH_3) = 1.15\ 10^{-12}$ cm^3 molecule^{-1} s^{-1},[17] whereas the rate coefficient for $Cl + CH_3CH_2C(O)OCH_3$ is around an order of magnitude lower than for the $Cl + CH_3CH_2CH_3$ reaction: $k(Cl + CH_3CH_2CH_3) = 13.7\ 10^{-11}$ cm^3 molecule^{-1} s^{-1}[1].[7] Despite this difference in reactivity trends, the measured distribution yields from the Cl-atom initiated oxidation of $CH_3CH_2C(O)OCH_3$ is similar to that obtained by using structure–activity relationships for OH radical attack on methyl propionate (see atmospheric implications section). This can probably be attributed to the differences in the reaction mechanisms. Whereas the interactions of Cl atoms with propane and methyl propionate and OH with propane are direct H-atom abstraction reactions, it is quite probable that the reaction of OH with methyl propionate proceeds via a cyclic transition state involving a carbonyl and methylene group which causes an enhancement in the OH reactivity toward this compound. Such behavior has been suggested to explain the enhanced reactivity observed in the reaction of OH with, for example, acetals[20] and ketones.[21,22] This enhanced kinetic reactivity would appear to influence the reactivity of the various sites toward OH attack such that the predicted product distribution using structure–activity relationships is not too dissimilar to that observed here for the reaction of Cl with methyl propionate.

3.3. Product Study of the Cl-Atom Initiated Oxidation of Methyl Propionate. The products of the Cl-atom initiated oxidation of methyl propionate were studied by the UV irradiation of methyl propionate/Cl_2/NO/air mixtures. Initial concentrations were as follows: Cl_2, 3×10^{14}; NO, 6×10^{14}; and methyl propionate, 3×10^{14} molecule cm^{-3}. The mixtures were irradiated for 1–10 min, leading to methyl propionate consumptions of approximately 40%.

With NO in the reaction system, OH radicals can be generated; however, the contribution of OH to the decay of methyl propionate is considered minimal. The steady-state concentrations of chlorine atoms generated in the experiments are ca. 10^8 molecule cm^{-3}, and the concentrations of OH radicals generated in the system in the presence of NO are expected to be $\approx 10^7$ molecule cm^{-3} from comparison with other hydrocarbon-NO_x systems. Combining these values with the measured rate constants for the reaction of chlorine atoms and OH radicals with methyl propionate shows that reaction of Cl atoms with methyl propionate outweighs reaction with OH by a factor of 100 or more.

By virtue of their characteristic IR spectra, propionic formic anhydride, propionic acid, CO, methyl pyruvate, acetaldehyde, methoxy formylperoxynitrate, formaldehyde, and methyl glyoxylate were identified among the degradation products. Figures 6 and 7 show the observed formation of propionic formic anhydride, propionic acid, methyl pyruvate, and methyl glyoxylate versus loss of methyl propionate. The linearity of the propionic formic anhydride, propionic acid, methyl pyruvate, and methyl glyoxylate products plots in Figures 6 and 7 suggests that these species are formed as primary products during the oxidation of methyl propionate and are not lost to any significant extent via secondary reactions. Least-squares analyses of these data give the product yields listed in Table 2.

Molar product yields of 0.132 ± 0.026 and 0.077 ± 0.015 given, in Table 2, for CO and acetaldehyde, respectively, refer to the early stage of the reaction, when secondary processes can largely be neglected. In the case of formaldehyde, secondary formation and removal processes occurring in the system under the experimental conditions employed render a reliable determination of its molar formation yield difficult. In the product

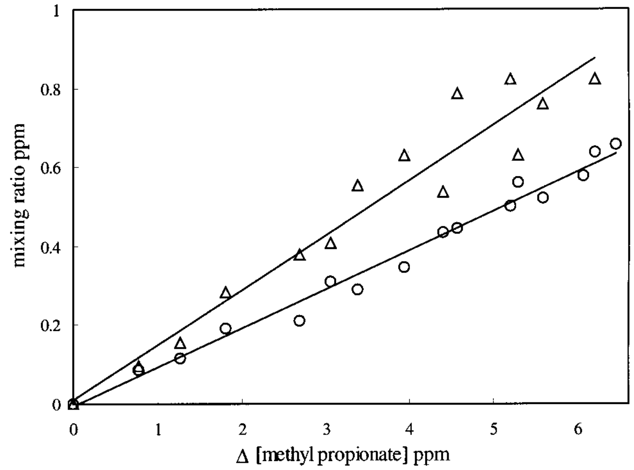


Figure 6. Formation of propionic formic anhydride (circles) and propionic acid (squares) versus loss of methyl propionate observed following the Cl-atom initiated oxidation of methyl propionate in air in the presence of NO_x.

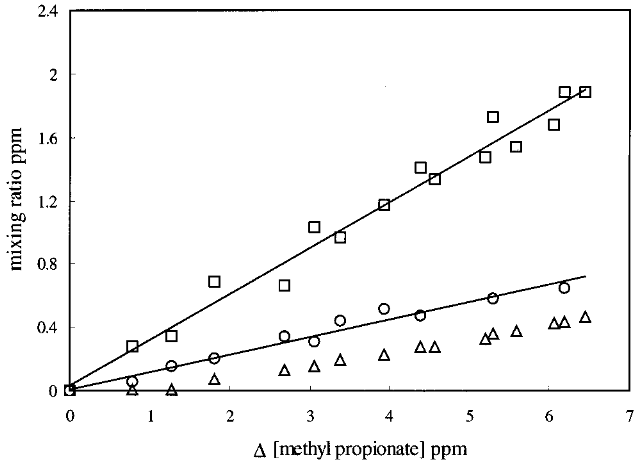


Figure 7. Formation of methyl glyoxylate (circles) and methyl pyruvate (squares) versus loss of methyl propionate observed following the Cl-atom initiated oxidation of methyl propionate in air in the presence of NO_x. The methoxy formylperoxynitrate (triangles) data plot shows curvature due to changes in the NO/NO_2 ratio during the experiment (see text).

TABLE 2: Observed Molar Product Yields in the Cl-Atom Initiated Oxidation of Methyl Propionate in the Presence of NO_x

product of methyl propionate	molar yields[a]
propionic formic anhydride	0.099 ± 0.019
propionic acid	0.139 ± 0.027
carbon monoxide	0.132 ± 0.026
methyl pyruvate	0.289 ± 0.057
acetaldehyde	0.077 ± 0.015
methoxy formylperoxynitrate	0.083 ± 0.016
methyl glyoxylate	0.111 ± 0.022

[a] Errors are the total overall estimated uncertainty of 20%.

analysis distinctive spectral features at 1835, 1748, 1308, 1237, and 799 cm^{-1} remain in the residual spectra after subtraction of all identified products. By comparison to literature spectra, these characteristic absorptions can be assigned to methoxy formylperoxynitrate, $CH_3OC(O)OONO_2$.[23,24] The formation of this compound is dependent on the NO/NO_2 ratio in the experimental system and, consequently, its yield is low at the beginning of the experiment when the NO/NO_2 ratio is high and increases gradually during the course of the experiment as the NO/NO_2 ratio becomes smaller (see Figure 7). An estimation of the concentration of the peroxynitrate has been made using the value of 4.43×10^{-19} cm^2 $molecule^{-1}$ (base 10) for the absorption cross section of acetylperoxynitrate at 1835 cm^{-1} available in the literature;[25] its molar formation yield was found to be 0.083 ± 0.016 at the end of the experiments.

The residual product spectra also show the presence of $RONO_2$-type bands at approximately 1670, 1300, and 845 cm^{-1}. The specific $RONO_2$ product(s) formed could not be identified. However, an estimate of the molar $RONO_2$ concentration was made from the integrated intensity of the 1670 cm^{-1} absorption band and the average integrated absorption coefficient of $(2.5 \pm 0.2) \times 10^{-17}$ cm $molecule^{-1}$ (base10) reported in the literature for the corresponding band of other organic nitrates.[34] Using this value, the average $RONO_2$ molar formation yield obtained from two experiments was 7 ± 2%; the estimated total error includes uncertainties associated with the absorption coefficient.

There are two possible sources of organic nitrates in the present experiments; the nitrate channel of the reaction of peroxy radicals with NO (12b), or the association reaction of alkoxy radicals with NO_2 (13).

$$RO_2 + NO \rightarrow RO + NO_2 \tag{12a}$$

$$RO_2 + NO + M \rightarrow RONO_2 + M \tag{12b}$$

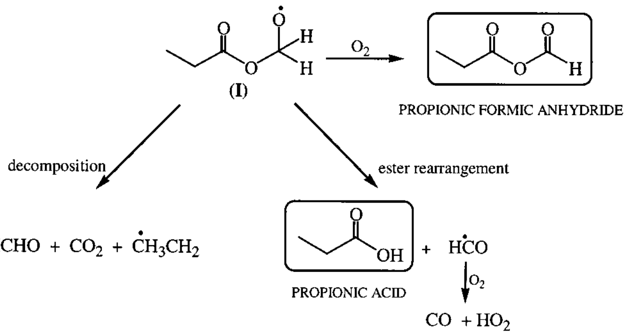
$$RO + NO_2 + M \rightarrow RONO_2 + M \tag{13}$$

Within the experimental uncertainties, the organic nitrate(s) product features at 1670, 1300, and 845 cm^{-1} were observed to increase linearly with methyl propionate consumption. During the experiment, the NO_2 concentration substantially increased from essentially zero prior to the first irradiation to $4-6 \times 10^{14}$ molecule cm^{-3} at the end of the experiment. The linearity of the $RONO_2$ formation suggests that reaction 12b rather than reaction 13 is the source of the observed $RONO_2$. Accordingly, we can estimate an effective upper limit for the branching ratio of $k_{12b}/(k_{12a} + k_{12b}) = 0.07 \pm 0.02$ for the mixture of the three different peroxy radicals formed following Cl attack on methyl propionate in the presence of O_2.

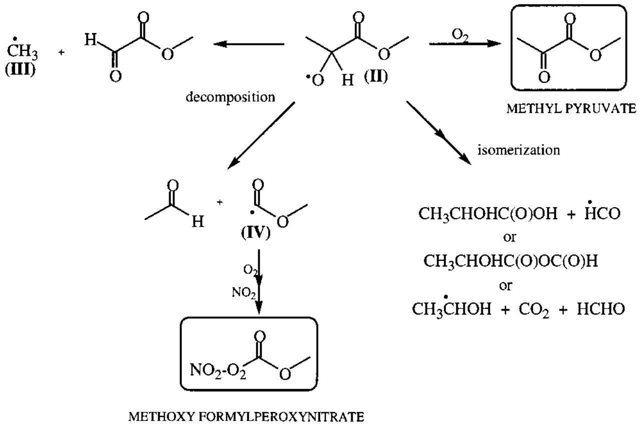
The reaction of peroxy radicals with NO is believed to involve the formation of a short-lived ROONO complex which can either decompose to give RO and NO_2 or rearrange to give the nitrate $RONO_2$.[26] With increasing size of the R moiety, the importance of the $RONO_2$ producing channel increases ($R = CH_3$, $k_{12b}/(k_{12a} + k_{12b}) < 0.01$,[27,28] $R = C_3H_7$, $k_{12b}/(k_{12a} + k_{12b}) = 0.036$;[29] R = *tert*-butyl, $k_{12b}/(k_{12a} + k_{12b}) = 0.18$,[30] $R = C_6H_{11}$, $k_{12b}/(k_{12a} + k_{12b}) = 0.22$[29]). Methyl propionate has six "heavy" atoms and has a molecular weight which is comparable to that of hexane. It is interesting to note that the nitrate forming channel of the RO_2 + NO reactions occurring during the oxidation of methyl propionate is substantially (approximately a factor of 3) less important than that in the corresponding reactions of alkyl peroxy radicals of the same size. This observation is similar to recent findings for halogenated peroxy radicals which, when compared to unsubstituted alkyl peroxy radicals, produce a much lower nitrate yield in their reactions with NO.[31] It appears that the electron withdrawing influence of the oxygen or halogen substitutents act to reduce the branching ratio $k_{12b}/(k_{12a} + k_{12b})$. The factors governing the nitrate yields in reaction 12 are poorly understood and need further study.

As discussed above, the reaction of Cl atoms with methyl propionate, $CH_3CH_2C(O)OCH_3$, can proceed by H-atom abstraction from all three of the hydrogenated carbons in the molecule. In one atmosphere of air the alkyl radicals formed

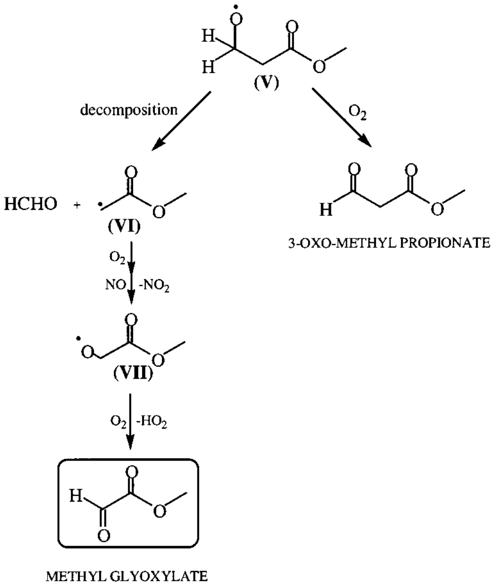
SCHEME 1



SCHEME 2

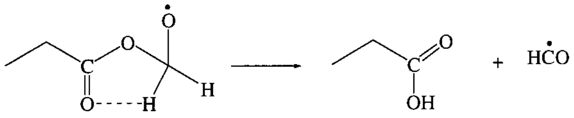


SCHEME 3



after the H-atom abstraction react solely with O_2 to form the corresponding alkyl peroxy radicals.[17,32] Reaction with NO then leads to formation of the analogous alkoxy radicals. The product observed following UV irradiation of methyl propionate/Cl_2/NOx/air mixtures provide insight into the atmospheric fate of the alkoxy radicals formed during the atmospheric oxidation of methyl propionate in the presence of NO_x. The possible reaction channels for each of the 3 alkoxy radicals are outlined in Schemes 1−3. These schemes form the basis for the following discussion. The different products identified from the reactions of the three alkoxy radicals are enclosed in boxes in the reaction schemes. The reaction products highlighted in Schemes 1−3 account for 71.6 ± 14.3% C. When the organic nitrate yield is included, the observed products account for 79 ± 16% C.

3.4. Atmospheric Fate of $CH_3CH_2C(O)OCH_2O\cdot$ Radicals. Scheme 1 shows possible fates of the $CH_3CH_2C(O)OCH_2O\cdot$ **(I)** alkoxy radical. The observation in the present work of the formation of equivalent amounts of propionic acid and CO shows that the $CH_3CH_2C(O)OCH_2O\cdot$ radical undergoes an α ester-rearrangement (first observed by Tuazon et al.[33] for ethyl acetate). In the α ester-rearrangement one of the hydrogens bound to the carbon attached to the alkoxy radical center is transferred to the carbonyl oxygen associated with the ester functionality.



The formyl radical formed in the rearrangement reacts with O_2 to give CO. The observation of propionic formic anhydride shows that the bimolecular reaction with O_2 competes with α ester-rearrangement for the available $CH_3CH_2C(O)OCH_2O\cdot$ radicals. A similar competition was reported by Christensen et al.[15] for the analogous alkoxy radicals formed during the atmospheric oxidation of methyl acetate, $CH_3C(O)OCH_2O\cdot$. It is interesting to note that the relative importance of α ester-rearrangement versus bimolecular reaction with O_2 reported by Christensen et al.[15] for $CH_3C(O)OCH_2O\cdot$ radical, (65 ± 14)/(35 ± 5) = 1.9 ± 0.7, is indistinguishable from that observed here for $CH_3CH_2C(O)OCH_2O\cdot$ radical, (0.139 ± 0.027)/(0.099 ± 0.019) = 1.4 ± 0.7.

In Scheme 1, we have not included the possible decomposition of the alkoxy radical via C−O bond scission to the $CH_3CH_2C(O)\cdot$ radical and HCHO. There are two reasons why we have not included this possibility. First, the observed products can be explained without invoking this reaction channel. Second, in studies of the atmospheric fates of structurally analogous alkoxy radicals derived from methyl acetate ($CH_3C(O)OCH_2O\cdot$),[15] dimethyl glutarate ($CH_3OC(O)CH_2CH_2CH_2C(O)OCH_2O\cdot$),[34] and dimethyl succinate ($CH_3OC(O)CH_2CH_2C(O)OCH_2O\cdot$) [unpublished work from Wuppertal], no evidence of HCHO elimination has been observed. By analogy to the reported behavior of structurally similar radicals it seems unlikely that decomposition via C−O bond scission is significant for the $CH_3CH_2C(O)OCH_2O\cdot$ radical.

We conclude that the fate of $CH_3CH_2C(O)OCH_2O\cdot$ radicals formed in the atmospheric oxidation of methyl propionate in the presence of NO_x is α ester-rearrangement and reaction with O_2 with $k_{14}/(k_{15}[O_2]) = 1.4$.

$$CH_3CH_2C(O)OCH_2O\cdot \rightarrow CH_3CH_2C(O)OH + HCO \quad (14)$$

$$CH_3CH_2C(O)OCH_2O\cdot + O_2 \rightarrow CH_3CH_2C(O)OC(O)H + HO_2\cdot \quad (15)$$

3.5. Atmospheric Fate of $CH_3CH(O\cdot)C(O)OCH_3$ Radicals. As shown in Scheme 2, the alkoxy radical $CH_3CH(O\cdot)C(O)OCH_3$ **(II)**, formed after the H-atom abstraction from the $-CH_2C(O)O-$ entity, can react with O_2 to form methyl pyruvate, decompose via C−C bond cleavage, or undergo isomerization. The bond cleavage can proceed by two pathways, producing either methyl glyoxylate plus the $\cdot CH_3$ **(III)** radical or acetaldehyde plus the $\cdot C(O)OCH_3$ radical **(IV)**. Because of the greater stability of the $\cdot C(O)OCH_3$ radical compared to the methyl radical,[35,36] the channel producing acetaldehyde and the $\cdot C(O)OCH_3$ radical is predicted to dominate.

The observation of a substantial yield of methyl pyruvate shows that reaction with O_2 is an important fate of $CH_3CH(O\cdot)C(O)OCH_3$ radicals. In addition, the observation of comparable yields of acetaldehyde and methoxy formylperoxynitrate suggests that decomposition to the $CH_3CH(O\cdot)C(O)OCH_3$ radical to give a $\cdot C(O)OCH_3$ radical and CH_3CHO is also significant. The yield of acetaldehyde was observed to decrease for methyl propionate consumptions greater than 15−20%. We attribute this observation to secondary loss of acetaldehyde via reaction with Cl atoms which occurs with a rate constant of 7.8×10^{-11} [37] cm^3 $molecule^{-1}$ s^{-1} by H-atom abstraction from the -CHO group forming the $CH_3C(O\cdot)$ acyl radical, which then adds O_2 to form the acyl peroxyl radical. In the presence of NO_x, the acyl peroxyl radical can add NO_2 to form peroxylacetyl nitrate (PAN).[17] Under our experimental conditions, the major pathway of the methoxy formyl radical **(IV)** is expected to be the addition of O_2 and the further reaction with NO_2 to form methoxy formylperoxynitrate, rather than decomposition to CO_2 and $\cdot CH_3$.[38] The alkoxy radical $CH_3CH(O\cdot)C(O)OCH_3$ **(II)** can also undergo a 1,5-H shift isomerization via a six-membered transition state. Unfortunately, due to a lack of an infrared spectrum of the expected isomerization product, we are unable to determine if this process is occurring.

We conclude that the atmospheric fate of the $CH_3CH(O\cdot)C(O)OCH_3$ radical is reaction with O_2 to give methyl pyruvate and decomposition via C−C bond cleavage to give a $\cdot C(O)OCH_3$ radical and CH_3CHO with $(k_{16}[O_2])/k_{17} = 29/8 = 3.6$.

$$CH_3CH(O\cdot)C(O)OCH_3 + O_2 \rightarrow CH_3C(O)C(O)OCH_3 + HO_2\cdot \quad (16)$$

$$CH_3CH(O\cdot)C(O)OCH_3 \rightarrow CH_3CHO + \cdot C(O)OCH_3 \quad (17)$$

3.6. Atmospheric Fate of $\cdot OCH_2CH_2C(O)OCH_3$ Radicals. The alkoxy radical $\cdot OCH_2CH_2C(O)OCH_3$ (**V**) shown in Scheme 3 cannot form a six-membered transition state for isomerization via internal H-atom abstraction, and hence we need only consider reaction with O_2 and decomposition via C−C bond scission as fates for the alkoxy radical. Reaction of the $\cdot OCH_2CH_2C(O)OCH_3$ alkoxy radical **(V)** with O_2 will lead to the formation of 3-oxo-methyl propionate. We do not have a reference spectrum for 3-oxo-methyl propionate, and so we are unable to search for IR product features from this compound. However, after subtraction of IR features attributable to all the identified products (propionic formic anhydride, propionic acid, methyl pyruvate, methyl glyoxylate, acetaldehyde, and methoxy formylperoxynitrate), residual features remain which suggest the possible presence of 3-oxo-methyl propionate. Decomposition of $\cdot OCH_2CH_2C(O)OCH_3$ **(V)** leads to the formation of formaldehyde plus the $\cdot CH_2C(O)OCH_3$ radical **(VI)**. The $\cdot CH_2C(O)OCH_3$ radical will add O_2 and react with NO to give the $\cdot OCH_2C(O)OCH_3$ alkoxy radical. As discussed in the Experimental Section, control experiments employing the photolysis of methyl bromoacetate in mixtures of air in the presence of NO showed that in one atmosphere of air the fate of $\cdot OCH_2C(O)OCH_3$ radicals is mainly reaction with O_2 to give methyl glyoxalate. As seen from Table 2, methyl glyoxalate was an observed product with a molar yield of 0.11. As shown in Schemes 2 and 3, methyl glyoxalate can be formed following the decomposition of both $CH_3CH(O\cdot)C(O)OCH_3$ and $\cdot OCH_2CH_2C(O)OCH_3$ radicals. As described in the previous section, we believe that the fate of $CH_3CH(O\cdot)C(O)OCH_3$ radicals is dominated by reactions 16 and 17, and hence we choose to assign the observed methyl glyoxalate product to decomposition of $\cdot OCH_2CH_2C(O)OCH_3$ radicals via elimination of HCHO as illustrated in Scheme 3. This is also supported by results from product studies on the OH-radical and Cl-atom initiated oxidation of dimethyl succinate $CH_3OC(O)CH_2CH_2C(O)OCH_3$, performed in our laboratory.[39]

Because of the lack of positive evidence for the formation of 3-oxo methyl propionate, we recommend that for purposes of modeling the atmospheric chemistry of methyl propionate the sole fate of $\cdot OCH_2CH_2C(O)OCH_3$ is decomposition:

$$\cdot OCH_2CH_2C(O)OCH_3 \rightarrow HCHO + \cdot CH_2C(O)OCH_3 \quad (18)$$

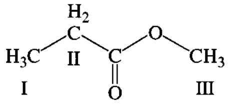
4. Implications for Atmospheric Chemistry

The atmospheric degradation of organic compounds is initiated by reaction with OH radicals, Cl atoms, ozone, NO_3 radicals, photolysis, and wet/dry deposition. Methyl propionate does not contain any unsaturated $>C{=}C<$ bonds and is therefore expected to react extremely slowly, if at all, with ozone and NO_3 radicals. As discussed by Notario et al.,[14] for typical atmospheric concentrations of Cl atoms and OH radicals, reaction with Cl atoms is a negligible loss process of $CH_3CH_2C(O)OCH_3$ compared to reaction with OH radicals.

Esters have low Henry's law coefficients ($K_H = 8$ M atm^{-1} for methyl acetate,[40] $K_H = 6.1$ M atm^{-1} for methyl propionate[41]); and in general for species with Henry's law constants smaller than 400 M atm^{-1}, it can be calculated that less than 1% of their mass is dissolved in the aqueous phase inside a cloud. This suggests that such species reside mainly in the gas phase in the atmosphere and precludes wet deposition from being a significant atmospheric loss mechanism for methyl propionate.

Photolysis of esters appears to be only important below 240 nm[42] and will not be of any significance in the lower atmosphere. As discussed in section 3.2, we recommend k(OH + methyl propionate) $= 9.3 \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. Assuming an atmospheric lifetime for methyl chloroform with respect to reaction with OH of 5.9 years[43] and $k(OH + CH_3CCl_3) = 7.0 \times 10^{-15}$ cm^3 $molecule^{-1}$ s^{-1} [13] leads to an estimate for the atmospheric lifetime of $CH_3CH_2C(O)OCH_3$ against reaction with OH of 16 days.

The atmospheric oxidation of methyl propionate is initiated by reaction with OH radicals. Using structure−activity relationships it can be estimated that the relative importance of OH attack on the three possible sites is 25% (**I**), 43% (**II**), and 32% (**III**).[44,45]



The OH radical reaction will produce three alkyl radicals which will add O_2 to give peroxy radicals.

$$CH_3CH_2C(O)OCH_2\cdot + O_2 + M \rightarrow CH_3CH_2C(O)OCH_2OO\cdot + M$$

$$CH_3CH(\cdot)C(O)OCH_3 + O_2 + M \rightarrow CH_3CHOO(\cdot)C(O)OCH_3 + M$$

$$\cdot CH_2CH_2C(O)OCH_3 + O_2 + M \rightarrow \cdot OOCH_2CH_2C(O)OCH_3 + M$$

For conditions prevailing in polluted urban air masses the dominant fate of the peroxy radicals will be reaction with NO leading to alkoxy radicals as the major products with small amounts of organic nitrates (7%). From the results presented in sections 3.4−3.6 we recommend that for the purposes of modeling oxidant formation in urban air masses, the atmospheric chemistry of methyl propionate be represented as

$$\begin{gathered}\mathrm{OH} + \mathrm{CH_3CH_2C(O)OCH_3} + 1.32\ \mathrm{NO} \rightarrow 0.07\ \mathrm{RONO_2} + \\ 0.32\ \mathrm{HCHO} + 0.23\ \mathrm{HC(O)C(O)OCH_3} + 0.93\ \mathrm{HO_2}^{\bullet} + \\ 0.32\ \mathrm{CH_3C(O)C(O)OCH_3} + 0.09\ \mathrm{CH_3CHO} + \\ 0.09\ \mathrm{CO_2} + 0.17\ \mathrm{CH_3CH_2C(O)OH} + 0.17\ \mathrm{CO} + \\ 0.12\ \mathrm{CH_3CH_2C(O)OC(O)H} + 1.25\ \mathrm{NO_2}\end{gathered}$$

In the derivation of the above equation we assume that the 7% organic nitrate yield is composed of 3% $CH_3CH_2C(O)OCH_2$-ONO_2, 2% $CH_3CH(ONO_2)C(O)OCH_3$, and 2% O_2NOCH_2-$CH_2C(O)OCH_3$ and that the fate of $^{\bullet}C(O)OCH_3$ radicals is addition of O_2, reaction with NO, and decomposition to give CO_2 and CH_3O radicals. The overall reactivity of methyl propionate toward OH radicals is low compared to conventional solvents such as chlorocarbon aromatic and unsubstituted hydrocarbon based solvents and the bulk of the oxidation of methyl propionate produces multifunctional oxygenated compounds such as $HC(O)C(O)OCH_3$, $CH_3C(O)C(O)OCH_3$, and $CH_3CH_2C(O)OH$ which have a lower reactivity toward OH radicals than the parent compound. Methyl propionate has a low atmospheric reactivity with respect to oxidant formation.

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