J. Phys. Chem. A **2000,** *104,* 345−351

Atmospheric Oxidation Mechanism of Methyl Acetate

L. K. Christensen,* J. C. Ball, and T. J. Wallington*,†

Ford Research Laboratory, SRL-3083, Ford Motor Company, P.O. Box 2053, Dearborn, Michigan 48121-2053

Received: September 2, 1999; In Final Form: November 9, 1999

Smog chamber/FTIR techniques were used to study the Cl atom initiated oxidation of $CH_3C(O)OCH_3$ in 700 Torr of N_2/O_2 at 296 K. Relative rate techniques were used to measure $k(Cl+CH_3C(O)OCH_3) = (2.2 \pm 0.3) \times 10^{-12}$, $k(Cl+CH_3C(O)CH_3) = (2.2 \pm 0.4) \times 10^{-12}$, $k(Cl+CH_3C(O)OC(O)H) = (1.0 \pm 0.1) \times 10^{-13}$, and $k(Cl+ ClCH_2C(O)OCH_3) = (8.5 \pm 1.9) \times 10^{-13}$ cm^3 molecule^{-1} s^{-1}. The reaction of $Cl+CH_3C(O)OCH_3$ was found to proceed more than 95% via H-abstraction at the $-OCH_3$ site. The fate of the $CH_3C(O)OCH_2O\cdot$ radical was studied in 700 Torr of N_2/O_2 diluent at 296 K in the absence and presence of NO. Two loss mechanisms were identified: reaction with O_2 to give $CH_3C(O)OC(O)H$ and α-ester rearrangement to give $CH_3C(O)OH$ and $HCO\cdot$ radicals. It was found that α-ester rearrangement is more likely when $CH_3C(O)OCH_2O\cdot$ radicals were produced via the $CH_3C(O)OCH_2O_2\cdot + NO$ reaction than when they were produced via the self-reaction of peroxy radicals. In one atmosphere of air ($[O_2] = 160$ Torr) containing NO at 296 K it can be calculated that 65 ± 14% of the $CH_3C(O)OCH_2O\cdot$ radicals undergo α-ester rearrangement while 35 ± 5% react with O_2.

1. Introduction

Esters are widely used in industry as solvents and during the manufacture of perfumes and food flavoring. They are volatile organic compounds (VOCs) and may be released into the atmosphere during their use (methyl acetate has a vapor pressure of 28.8 kPa at 298 K). 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. Methyl acetate is produced during the atmospheric degradation of *tert*-amyl methyl ether (TAME) in a molar yield of 35%,[1] and from methyl *tert*-butyl ether (MTBE) in a molar yield of 15%.[2,3] Despite their importance, the atmospheric oxidation mechanism of esters has received relatively little attention. To improve our understanding of the atmospheric chemistry of esters we report here the results of a study of the Cl atom initiated oxidation of methyl acetate.

The atmospheric oxidation of methyl acetate is initiated by reaction with OH radicals:

$$CH_3C(O)OCH_3 + OH \rightarrow CH_3C(O)OCH_2\cdot + H_2O \qquad (1a)$$

$$CH_3C(O)OCH_3 + OH \rightarrow \cdot CH_2C(O)OCH_3 + H_2O \qquad (1b)$$

Under atmospheric conditions alkyl radicals produced in reaction 1 react with oxygen to give peroxy radicals:

$$CH_3C(O)OCH_2\cdot + O_2 \rightarrow CH_3C(O)OCH_2O_2\cdot \qquad (2)$$

$$\cdot CH_2C(O)OCH_3 + O_2 \rightarrow \cdot O_2CH_2C(O)OCH_3 \qquad (3)$$

Peroxy radicals react with NO, NO_2, HO_2, and other peroxy radicals in the atmosphere.[4] Reaction with NO dominates in polluted air masses and is expected to give largely, if not exclusively, the corresponding alkoxy radical. In this work we have studied the fate of the $CH_3C(O)OCH_2O\cdot$ radical.

2. Experimental Section

All experiments were performed in a 140-liter Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer.[5] The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) used to photochemically initiate the experiments. The oxidation of $CH_3C(O)OCH_3$ was initiated by reaction with Cl atoms generated by photolysis of molecular chlorine in 700 Torr of O_2/N_2 diluent at 296 ± 2 K

$$Cl_2 + h\nu \rightarrow 2\,Cl \qquad (4)$$

$$Cl + CH_3C(O)OCH_3 \rightarrow \text{products} \qquad (5)$$

Loss of $CH_3C(O)OCH_3$ and formation of products were monitored by Fourier transform infrared spectroscopy using an infrared path length of 28 m and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 to 128 co-added interferograms.

Calibration of $ClCH_2C(O)OC(O)H$, $CH_3C(O)OC(O)H$, $CH_3C(O)OH$, and CO reference spectra was achieved by expanding known volumes of these compounds into the chamber. $CH_3C(O)OC(O)H$ was synthesized following the procedure of Schijf and Stevens.[6] Ultrahigh purity N_2, O_2, and air diluent gases were obtained from Michigan Airgas Corp. All other reagents were obtained from Aldrich Chemical Co. at purities >99%. During calibration of the $CH_3C(O)OH$ reference spectrum allowance was made for the presence of monomer and dimer in the vapor.[7]

In smog chamber experiments unwanted loss of reactants and products via photolysis, dark chemistry, and wall reactions has to be considered. Control experiments were performed to check for such unwanted losses of $ClCH_2C(O)OC(O)H$, $CH_3C(O)OCH_3$, $CH_3C(O)OC(O)H$, and $CH_3C(O)OH$. During 14 min of

---

[†] E-mail: twalling@ford.com.

10.1021/jp993127n CCC: $19.00

UV irradiation 13% loss of $ClCH_2C(O)OC(O)H$ was observed, from which a photolysis rate of 1.7×10^{-4} s^{-1} was calculated. No loss (<2%) of $CH_3C(O)OCH_3$, $CH_3C(O)OC(O)H$, or $CH_3C(O)OH$ was observed when these compounds were irradiated in air diluent, showing that photolysis and deposition on the chamber walls are not important. To check for hydrolysis of $CH_3C(O)OC(O)H$, reaction mixtures which had been subjected to photolysis (40−80% $CH_3C(O)OCH_3$ consumption) were left in the dark for 15−30 min; no loss of $CH_3C(O)OC(O)H$ was observed.

3. Results

3.1 Relative Rate Studies of the Reactions of Cl Atoms with $CH_3C(O)OCH_3$, $CH_3C(O)CH_3$, $CH_3C(O)OC(O)H$, and $ClCH_2C(O)OCH_3$. Prior to investigating the atmospheric oxidation products of $CH_3C(O)OCH_3$, relative rate experiments were performed to determine the kinetics of reactions 5, 6, 7, and 8. Initial concentrations used were 10−12 mTorr $CH_3C(O)OCH_3$, 9−39 mTorr $CH_3C(O)CH_3$, 3−6 mTorr $CH_3C(O)OC(O)H$, 4−9 mTorr $ClCH_2C(O)OCH_3$, 58−92 mTorr CH_3CH_2F, 35−240 mTorr CH_3Cl, 8−29 mTorr CH_3OCHO, 9−10 mTorr CH_4, 2−3 mTorr CH_3F, and 10−258 mTorr of Cl_2, in 700 Torr of air or N_2 diluent.

$$Cl + CH_3C(O)OCH_3 \rightarrow \text{products} \tag{5}$$

$$Cl + CH_3C(O)CH_3 \rightarrow \text{products} \tag{6}$$

$$Cl + CH_3C(O)OC(O)H \rightarrow \text{products} \tag{7}$$

$$Cl + ClCH_2C(O)OCH_3 \rightarrow \text{products} \tag{8}$$

Reaction 5 was measured relative to reactions 9, 10, and 11. Reaction 6 was measured relative to reactions 9, 10, 13, and 14. Reaction 7 was measured relative to reactions 10 and 12, and reaction 8 was measured relative to reaction 11

$$Cl + C_2H_5F \rightarrow \text{products} \tag{9}$$

$$Cl + CH_3Cl \rightarrow \text{products} \tag{10}$$

$$Cl + CH_3OC(O)H \rightarrow \text{products} \tag{11}$$

$$Cl + CH_4 \rightarrow \text{products} \tag{12}$$

$$Cl + CH_3F \rightarrow \text{products} \tag{13}$$

$$Cl + C_2H_5Cl \rightarrow \text{products} \tag{14}$$

The observed losses of $CH_3C(O)OCH_3$, $CH_3C(O)CH_3$, $CH_3C(O)OC(O)H$, and $ClCH_2C(O)OCH_3$ versus those of reference compounds in the presence of Cl atoms are shown in Figures 1 and 2. Rate constant ratios were derived from linear least-squares analysis of the data in Figures 1 and 2; results are shown in Table 1. Values of k_5, k_6, k_7, and k_8 were derived using $k_9 = 7.5 \times 10^{-12}$,[8] $k_{10} = 4.9 \times 10^{-13}$,[8] $k_{11} = 1.4 \times 10^{-12}$,[9] $k_{12} = 1.0 \times 10^{-13}$,[8] $k_{13} = 3.5 \times 10^{-13}$,[8] and $k_{14} = 8.04 \times 10^{-12}$.[10] We estimate that potential systematic errors associated with uncertainties in the reference rate constants add 10% uncertainty ranges for k_5, k_6, k_7, and k_8. We choose to cite final values of k_5, k_6, k_7, and k_8, which are the averages of the individual determinations given in Table 1. Hence, $k_5 = (2.2 \pm 0.3) \times 10^{-12}$, $k_6 = (2.2 \pm 0.4) \times 10^{-12}$, $k_7 = (1.0 \pm 0.1) \times 10^{-13}$, and $k_8 = (8.5 \pm 1.9) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1}. Quoted errors reflect both statistical uncertainties and potential systematic errors associated with the reference rate constants. Our value for k_5 is 23% lower than that of $k_5 = (2.85 \pm 0.35) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} reported in the absolute rate study by Notario et al.[11]

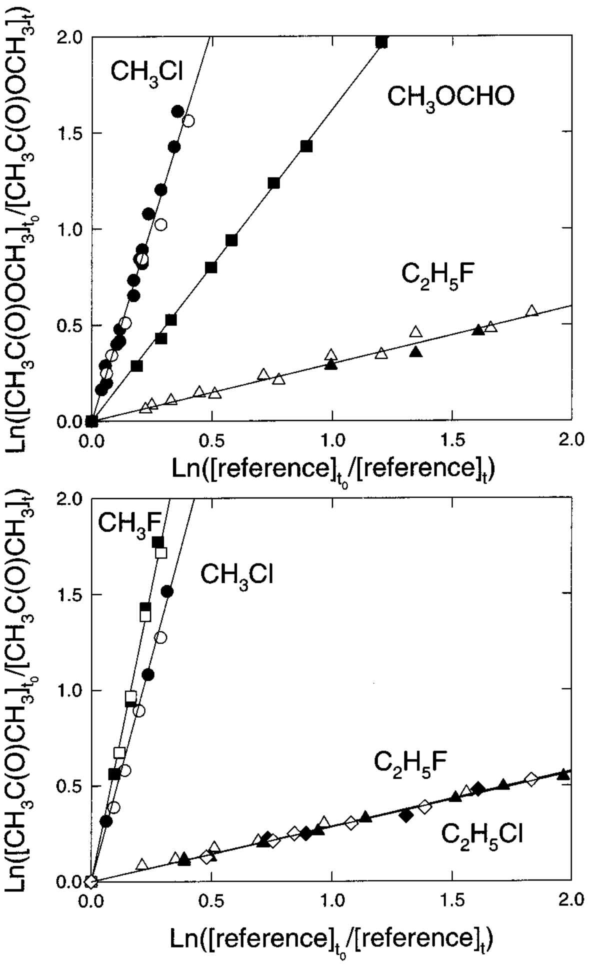


Figure 1. Upper panel: loss of $CH_3C(O)OCH_3$ versus C_2H_5F (triangles), CH_3Cl (circles), and $CH_3OC(O)H$ (squares) in the presence of Cl atoms in 700 Torr of air (open symbols) or N_2 (filled symbols) at 296 K. Lower panel: loss of acetone versus C_2H_5F (triangles), CH_3Cl (circles), CH_3F (squares), and C_2H_5Cl (diamonds). Experiments were performed at 296 K in 700 Torr of either O_2 (open symbols) or N_2 (filled symbols) diluent.

Two measurements of k_6 have been reported.[12,13] Wallington et al.[12] used the relative rate technique to measure $k_6/k(Cl + C_2H_5Cl) = 0.295 \pm 0.015$. Using $k(Cl + C_2H_5Cl) = 8.04 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, a value of $k_6 = 2.4 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1} was derived. As seen from Table 1, the results from the present work are consistent with the previous study at Ford.[12] Olsson et al. report a value of $k_6 = 1.7 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1},[13] which is 23% lower than that measured here. Potential systematic errors associated with the study of Olsson et al. have been discussed previously.[14] Based on the present work we recommend $k_6 = (2.2 \pm 0.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}.

3.2 Mechanism of the Reaction of Cl Atoms with $CH_3C(O)OCH_3$. To investigate the mechanism of reaction 5 experiments were performed using UV irradiation of $CH_3C(O)OCH_3/Cl_2/N_2$ mixtures. Initial concentrations were 0.7−5 Torr Cl_2 and 11−54 mTorr $CH_3C(O)OCH_3$ in 700 Torr of N_2. Reaction mixtures were subjected to 3−5 successive irradiations each having a duration of 2−5 s. In such experiments $ClCH_2C(O)$-

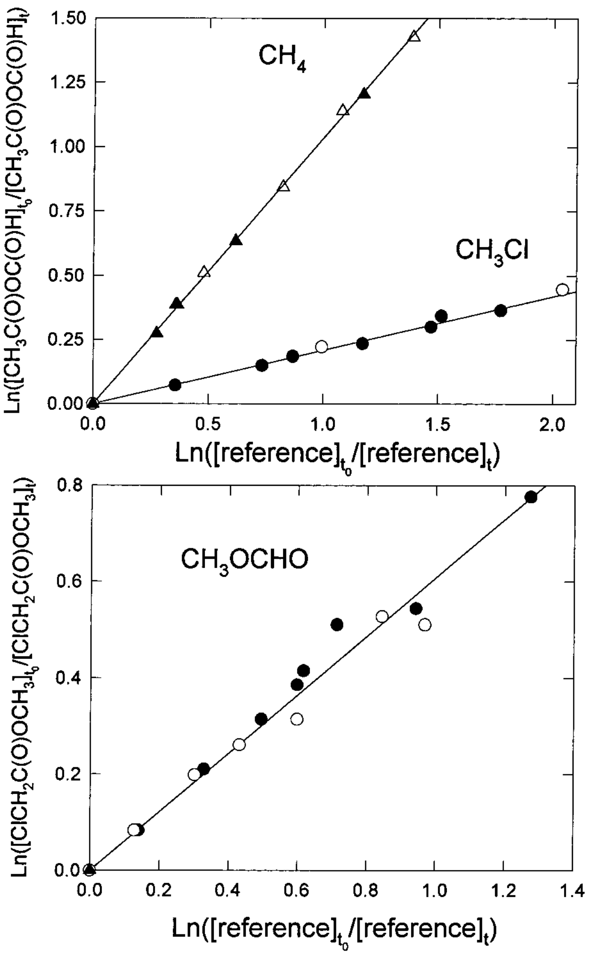


Figure 2. Upper panel: loss of $CH_3C(O)OC(O)H$ versus CH_4 (triangles), and CH_3Cl (circles) in the presence of Cl atoms in 700 Torr of O_2 (open symbols) or N_2 (filled symbols) at 296 K. Lower panel: loss of $ClCH_2C(O)OCH_3$ versus $CH_3OC(O)H$ in the presence of Cl atoms in 700 Torr of air (open symbols) or N_2 (filled symbols) at 296 K.

OCH_3 and $CH_3C(O)OCH_2Cl$ are produced by the following sequence of chain reactions:

$$Cl + CH_3C(O)OCH_3 \rightarrow CH_3C(O)OCH_2\cdot + HCl \quad (5a)$$

$$Cl + CH_3C(O)OCH_3 \rightarrow \cdot CH_2C(O)OCH_3 + HCl \quad (5b)$$

$$CH_3C(O)OCH_2\cdot + Cl_2 \rightarrow CH_3C(O)OCH_2Cl + Cl \quad (15a)$$

$$\cdot CH_2C(O)OCH_3 + Cl_2 \rightarrow ClCH_2C(O)OCH_3 + Cl \quad (15b)$$

The yield of $ClCH_2C(O)OCH_3$ provides a measure of the importance of channel 5b. With the short irradiation times used in these experiments, loss of $ClCH_2C(O)OCH_3$ due to photolysis is insignificant and reaction 8 is too slow to be a significant loss of $ClCH_2C(O)OCH_3$. There was no observable formation of $ClCH_2C(O)OCH_3$ following irradiation of $CH_3C(O)OCH_3$/Cl_2/N_2 mixtures. Using the calibrated reference spectrum of $ClCH_2C(O)OCH_3$ an upper limit for the $ClCH_2C(O)OCH_3$ yield of 5% was established. We conclude that $k_{5b}/(k_{5a} + k_{5b}) < 0.05$ and, by inference, $k_{5a}/(k_{5a} + k_{5b}) > 0.95$.

3.3 Fate of the $CH_3C(O)OCH_2O^{\bullet}$ Radical in the Absence of NO. To study the fate of the $CH_3C(O)OCH_2O\cdot$ radical, two sets of experiments were performed in which $CH_3C(O)OCH_3$/Cl_2/O_2 and $CH_3C(O)OCH_3$/Cl_2/O_2/NO mixtures were subjected to UV irradiation. In the first set of experiments the oxidation of methyl acetate was studied in the absence of NO. Initial concentrations of gas mixtures were 8−12 mTorr $CH_3C(O)OCH_3$ and 13−311 mTorr Cl_2. Experiments were performed at a constant total pressure of 700 Torr in N_2 diluent with the O_2 partial pressure varied over the range 0.9−700 Torr. Typical spectra obtained before (A) and after (B) UV irradiation of a mixture containing 11.6 mTorr $CH_3C(O)OCH_3$, 17 mTorr Cl_2, and 147 Torr O_2 are shown in Figure 3. In all experiments three products, $CH_3C(O)OC(O)H$, $CH_3C(O)OH$, and CO, were readily identified and quantified using calibrated reference spectra. In addition an unknown product(s) which absorbs at 830, 966, 1027, 1220, 1780, and 3581 cm^{-1} was observed, see Figure 3 panel G. As shown in Figure 4, the increase of $CH_3C(O)OC(O)H$, $CH_3C(O)OH$, and CO scaled linearly with the loss of $CH_3C(O)OCH_3$, suggesting that secondary loss or formation of these products is insignificant. In contrast, inspection of Figure 4 shows that the unknown product(s) is subject to secondary loss processes in the chamber. The yield of the unknown product was estimated from the initial rate of its formation by assuming that it accounts for the balance of the methyl acetate loss.

Reaction of Cl atoms with methyl acetate in the presence of O_2 gives rise to peroxy radicals

$$Cl + CH_3C(O)OCH_3 \rightarrow CH_3C(O)OCH_2\cdot + HCl \quad (5a)$$

$$CH_3C(O)OCH_2\cdot + O_2 \rightarrow CH_3C(O)OCH_2O_2\cdot \quad (2)$$

In the absence of NO, $CH_3C(O)OCH_2O\cdot$ radicals are formed by the peroxy radical self-reaction

$$2\ CH_3C(O)OCH_2O_2\cdot \rightarrow 2\ CH_3C(O)OCH_2O\cdot + O_2 \quad (16a)$$

$$2\ CH_3C(O)OCH_2O_2\cdot \rightarrow CH_3C(O)OC(O)H + CH_3C(O)OCH_2OH + O_2 \quad (16b)$$

There are several possible fates of the $CH_3C(O)OCH_2O\cdot$ radical. They can react with oxygen to form acetic formic anhydride, reaction 17. Tuazon et al.[15] have reported that alkoxy radicals of the structure $RC(O)OCHO\cdot R'$ can undergo α-ester rearrangement to $RC(O)OH$ plus $R'C(O)\cdot$. Evidence of α-ester rearrangement in $CF_3C(O)OCHO\cdot CF_3$ radicals has been reported.[16] In the case of $CH_3C(O)OCH_2O\cdot$ radicals α-ester rearrangement will give acetic acid and formyl radicals, reaction 18. The alkoxy radical could also decompose via C−O or C−H bond cleavage, reaction 19 or 20, and/or 1,5-H shift isomerization, reaction 21:

$$CH_3C(O)OCH_2O\cdot + O_2 \rightarrow CH_3C(O)OC(O)H + HO_2 \quad (17)$$

$$CH_3C(O)OCH_2O\cdot \rightarrow CH_3C(O)OH + HCO\cdot \quad (18)$$

$$CH_3C(O)OCH_2O\cdot \rightarrow CH_3C(O)O\cdot + CH_2O \quad (19)$$

$$CH_3C(O)OCH_2O\cdot \rightarrow CH_3C(O)OC(O)H + H \quad (20)$$

$$CH_3C(O)OCH_2O\cdot \rightarrow \cdot CH_2C(O)OCH_2OH \quad (21)$$

Yields of $CH_3C(O)OC(O)H$, $CH_3C(O)OH$, and CO observed from the Cl initiated oxidation of $CH_3C(O)OCH_3$ in the absence of NO are shown in Figure 5. The yield of $CH_3C(O)OC(O)H$ increases while the yield of $CH_3C(O)OH$ decreases with increasing oxygen concentration. This behavior reflects a competition between reactions 17 and 18. The observed CO

TABLE 1: Rate Constant Ratios for Reactions Involving Cl Atoms with Methyl Acetate, Acetone, Formic Acetic Anhydride, and Methyl Chloroacetate, Measured at 296 ± 2 K

	$CH_3C(O)OCH_3$		$CH_3C(O)CH_3$		$CH_3C(O)OC(O)H$		$ClCH_2C(O)OCH_3$	
ref	k_5/k_{ref}	$k_5{}^a$	k_6/k_{ref}	$k_6{}^a$	k_7/k_{ref}	$k_7{}^a$	k_8/k_{ref}	$k_8{}^a$
C_2H_5F	0.297 ± 0.032	22.3 ± 3.3	0.288 ± 0.017	21.6 ± 2.5				
CH_3Cl	4.09 ± 0.33	20.0 ± 2.6	4.69 ± 0.16	23.0 ± 2.4	0.209 ± 0.017	1.02 ± 0.13		
CH_3OCHO	1.62 ± 0.16	22.7 ± 3.2					0.61 ± 0.12	8.5 ± 1.9
CH_4					1.04 ± 0.05	1.04 ± 0.12		
CH_3F			6.15 ± 0.26	21.5 ± 2.3				
C_2H_5Cl			0.284 ± 0.018	22.8 ± 2.7				

[a] Units of 10^{-13} cm^3 molecule^{-1} s^{-1}, error limits include 10% uncertainty in k_{ref}.

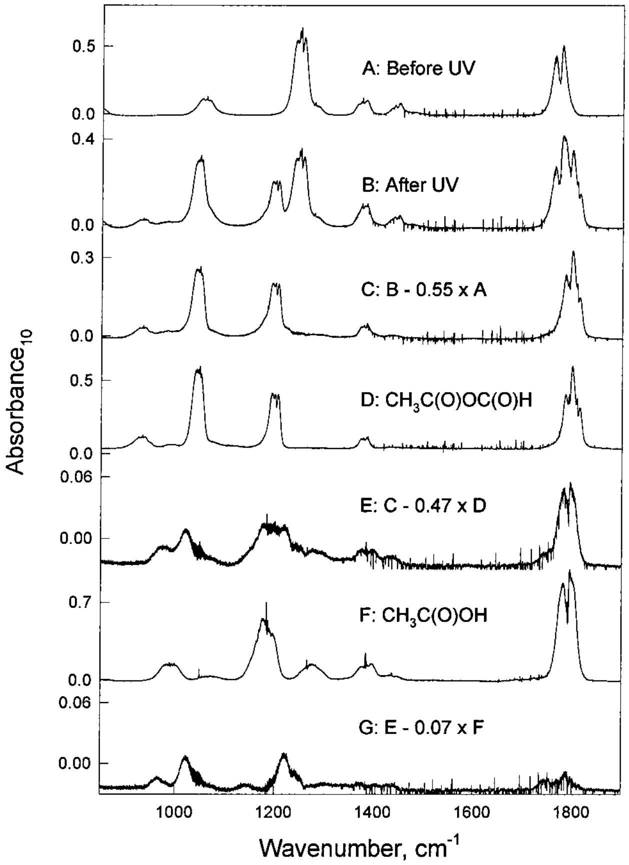


Figure 3. IR spectra before (A) and after (B) a 1 min irradiation of a mixture of 11.6 mTorr of $CH_3C(O)OCH_3$, 17 mTorr Cl_2, 147 Torr O_2, and 553 Torr of N_2. The consumption of $CH_3C(O)OCH_3$ was 45%. Panel C shows the product spectrum obtained after subtraction of features attributable to $CH_3C(O)OCH_3$ from panel B. Panel D shows the reference spectrum of $CH_3C(O)OC(O)H$. Panel E shows the residual after subtraction of features attributable to $CH_3C(O)OC(O)H$ from panel C. Panel F shows the reference spectrum of $CH_3C(O)OH$. Panel G shows the residual after subtraction of features attributable to CH_3C-(O)OH from panel E.

yield decreases with decreasing O_2 concentration in a similar fashion as $CH_3C(O)OH$. This is consistent with the formation of formyl radicals in reaction 18, which react with O_2 to give CO and HO_2. Measured yields of CO were always slightly (≈0.07) higher than the yields of $CH_3C(O)OH$, but this difference is not significant within the experimental uncertainty. Any $CH_3C(O)O^•$ radicals formed by reaction 19 will decompose to form CO_2 and $CH_3{}^•$ radicals. Methyl radicals will be oxidized to give HCHO, CH_3OH, and CH_3OOH. Due to their rapid reaction with Cl atoms (20−30 times faster than reaction 5) HCHO, CH_3OH, and CH_3OOH will be converted into CO. The consistency between the CO and $CH_3C(O)OH$ yields indicates that reaction 19 is insignificant. The combined yield of $CH_3C(O)OH$ and $CH_3C(O)OC(O)H$ accounts for approximately 80% of reacted $CH_3C(O)OCH_3$, see Figure 5.

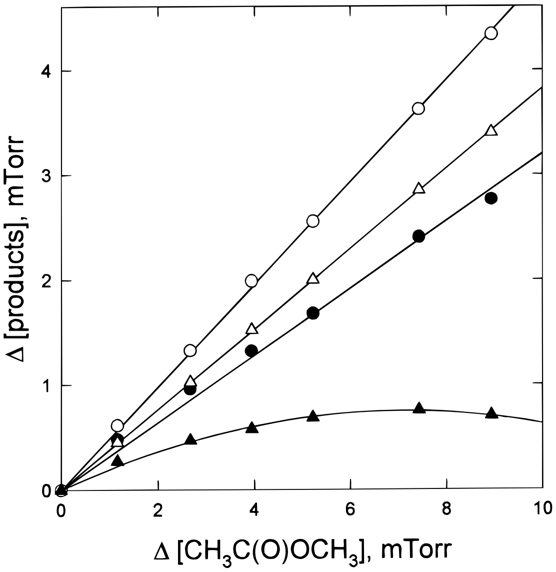


Figure 4. Formation of $CH_3C(O)OH$ (filled circles), $CH_3C(O)OC$-(O)H (open circles CO, (open triangles), and an unknown product believed to be $CH_3C(O)OCH_2OOH$ (filled triangles) versus loss of $CH_3C(O)OCH_3$, following UV irradiation of a mixture of 11.6 mTorr of $CH_3C(O)OCH_3$, 17 mTorr Cl_2, 147 Torr O_2, and 553 Torr of N_2. The straight lines are linear least-squares fits. The curve is a second-order regression to aid visual inspection of the data trend.

The $CH_3C(O)OC(O)H$ yield shows a nonzero *y*-axis intercept in Figure 5. There are several potential explanations for this: (i) reaction 20 could be important, (ii) the molecular channel of the peroxy radical self-reaction (channel 16b) could be significant, (iii) the anhydride could be formed in the HO_2 + $CH_3C(O)OCH_2O_2{}^•$ reaction (channel 22b)

$$CH_3C(O)OCH_2O_2{}^• + HO_2 \rightarrow CH_3C(O)OCH_2OOH + O_2 \qquad (22a)$$

$$CH_3C(O)OCH_2O_2{}^• + HO_2 \rightarrow CH_3(O)OC(O)H + H_2O + O_2 \qquad (22b)$$

Assuming that reactions 17 and 18 are the sole fate of CH_3C-(O)$OCH_2O^•$ radicals, the dependence of the $CH_3C(O)OCH_3$ and $CH_3C(O)OH$ yields on $[O_2]$ can be expressed in terms of the rate constant ratio k_{17}/k_{18}. The yield of $CH_3C(O)OC(O)H$ is given by

$$Y(CH_3C(O)OC(O)H) = Y(RO^•)\left(\frac{\frac{k_{17}}{k_{18}}[O_2]}{\frac{k_{17}}{k_{18}}[O_2] + 1}\right) + C \qquad (I)$$

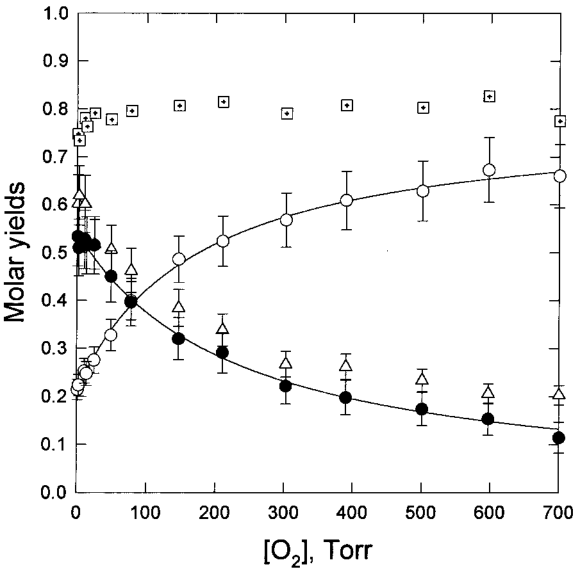


Figure 5. Yields of $CH_3C(O)OH$ (filled circles), $CH_3C(O)OC(O)H$ (open circles), CO (open triangles), and the combined yield of $CH_3C(O)OH$ and $CH_3C(O)OC(O)H$ (squares) versus the O_2 partial pressure following the UV irradiation of $CH_3C(O)OCH_3/Cl_2/N_2/O_2$ mixtures at 700 Torr total pressure and 296 K. Curves are least-squares fits of expressions I and II to the data, see text for details.

where $Y(RO\cdot)$ is the yield of the $CH_3C(O)OCH_2O\cdot$ radical. The term C in eq I accounts for formation of $CH_3C(O)OC(O)H$ via channels that are independent of O_2 concentration, i.e., via reaction 16b and/or 22b. The yield of $CH_3C(O)OH$ is given by

$$Y(CH_3C(O)OH) = Y(RO\cdot)\left(\frac{1}{\frac{k_{17}}{k_{18}}[O_2] + 1}\right) \qquad (II)$$

The curves in Figure 5 are least-squares fits of expressions I and II to the data. From the $CH_3C(O)OH$ data in Figure 5 we derive $k_{17}/k_{18} = 0.0045 \pm 0.0005$ Torr^{-1}, and $Y(RO\cdot) = 0.54 \pm 0.01$, while the $CH_3C(O)OC(O)H$ data gives $k_{17}/k_{18} = 0.0059 \pm 0.0010$ Torr^{-1}, $Y(RO\cdot) = 0.57 \pm 0.03$, and $C = 0.21 \pm 0.01$. The parameters derived from the $CH_3C(O)OH$ and $CH_3C(O)OC(O)H$ yields are consistent.

The unknown product shown in panel G in Figure 3 was not observed in the presence of NO (see section 3.4) suggesting that it is either $CH_3C(O)OCH_2OH$ formed by the self-reaction of the peroxy radicals or $CH_3C(O)OCH_2OOH$ formed in reaction 22. To distinguish between these two possibilities mixtures of 8.5–12.6 mTorr $CH_3C(O)OCH_3$, 96–277 mTorr Cl_2, 0.9–15 Torr H_2, and 131–136 Torr O_2 in 700 Torr N_2 diluent were introduced into the reaction chamber and irradiated using the UV fluorescent lamps. Experiments were performed where the initial concentration ratio $[H_2]/[CH_3C(O)OCH_3]$ was increased from 0 to 1800. The chlorine atoms react with $CH_3C(O)OCH_3$ and H_2 to give $CH_3C(O)OCH_2\cdot$ radicals and H atoms, which then add O_2 to give $CH_3C(O)OCH_2O_2\cdot$ and HO_2 radicals:

$$Cl + CH_3C(O)OCH_3 \rightarrow HCl + CH_3C(O)OCH_2\cdot \qquad (5a)$$

$$Cl + H_2 \rightarrow HCl + H \qquad (23)$$

Increasing the $[H_2]/[CH_3C(O)OCH_3]$ ratio increases the flux of HO_2 radicals in the system. This increases the importance of reaction with HO_2 and decreases the self-reaction as a loss mechanism for the peroxy radicals. The only products observed in these experiments were $CH_3C(O)OC(O)H$, $CH_3C(O)OH$, CO, and the unknown. As the $[H_2]/[CH_3C(O)OCH_3]$ ratio increased from 0 to 1800, the observed yield of the unknown increased by a factor of 2, suggesting that it is a hydroperoxide. The residual spectrum is consistent with that expected of a hydroperoxide. A very weak absorption feature is observed at 830 cm^{-1}, which is assigned to the OO stretching vibration. The observed feature at 3581 cm^{-1} is assigned to the O–H stretching vibration.

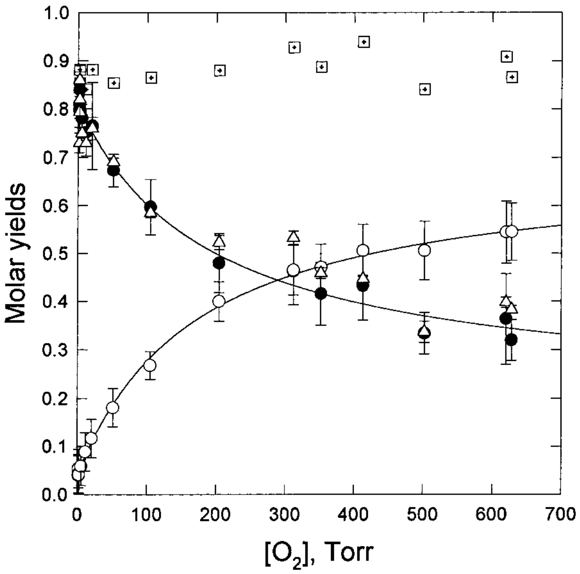


Figure 6. Yields of $CH_3C(O)OH$ (filled circles), $CH_3C(O)OC(O)H$ (open circles), CO (open triangles), and the combined yield of $CH_3C(O)OH$ and $CH_3C(O)OC(O)H$ (squares) versus the O_2 partial pressure following the UV irradiation of $NO/CH_3C(O)OCH_3/Cl_2/N_2/O_2$ mixtures at 700 Torr total pressure and 296 K. Curves are least-squares fits of expressions I and III to the data, see text for details.

3.4 Fate of the $CH_3C(O)OCH_2O^\bullet$ Radical in the Presence of NO. The oxidation of methyl acetate was also studied in the presence of NO. Initial concentrations used were 6–13 mTorr $CH_3C(O)OCH_3$, 6–185 mTorr Cl_2, and 3–14 mTorr NO. The experiments were performed at a constant total pressure of 700 Torr in N_2 diluent with the O_2 partial pressure varied over the range 1.8–628 Torr. In the presence of NO the $CH_3C(O)OCH_2O\cdot$ radicals are formed by reaction 24a:

$$CH_3C(O)OCH_2O_2\cdot + NO \rightarrow CH_3C(O)OCH_2O\cdot + NO_2 \qquad (24a)$$

$$CH_3C(O)OCH_2O_2\cdot + NO \rightarrow CH_3C(O)OCH_2ONO_2 \qquad (24b)$$

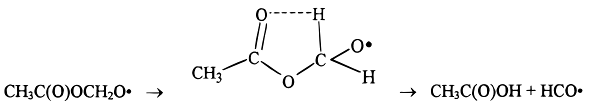
In all experiments $CH_3C(O)OC(O)H$, $CH_3C(O)OH$, and CO were identified and quantified using their calibrated reference spectra. The observed yields of the three products are plotted versus the O_2 concentration in Figure 6. The yield of $CH_3C(O)OH$ decreases with increasing oxygen concentration while the $CH_3C(O)OC(O)H$ yield increases. In the presence of NO, the $CH_3C(O)OCH_2O_2\cdot$ radicals are scavenged by reaction 24 and HO_2 radicals are scavenged by reaction with NO. A nonzero intercept in the $CH_3C(O)OC(O)H$ yield would be evidence of reaction 20. The intercept in the $CH_3C(O)OC(O)H$ yield is less than 0.05, and we conclude that reaction 20 is of minor importance.

In all experiments the $[NO]/[O_2]$ concentration ratio was kept below 5×10^{-3} to suppress possible formation of nitrites and nitrates via addition of NO or NO_2 to the alkoxy radicals. No change in the product yields were observed when the initial

NO concentration was decreased by a factor of 3 using high (620 Torr) and low (1.8 Torr) O_2 concentrations. Formation of nitrites or nitrates is of minor importance (less than 15%) for the data shown in Figure 6. The combined yields of $CH_3C(O)OC(O)H$ and $CH_3C(O)OH$ account for 87 ± 15% of the reacted methyl acetate.

A least-squares fit of equation I to the $CH_3C(O)OC(O)H$ data in Figure 6 gives $k_{17}/k_{18} = 0.0058 \pm 0.0009$ Torr^{-1}, $Y(RO\cdot) = 0.65 \pm 0.03$, and $C = 0.04 \pm 0.04$. The value of k_{17}/k_{18} derived here is consistent with that derived from the data in the absence of NO in Figure 5, but the yield of the alkoxy radical is significantly less than 100%. Comparison of the $CH_3C(O)OH$ data in Figures 5 and 6 shows that the $CH_3C(O)OH$ yield is uniformly higher in the presence of NO. In the presence of NO there appears to be a contribution to the $CH_3C(O)OH$ yield that is independent of the O_2 concentration.

A possible explanation for the experimental observations is that the reaction of $CH_3C(O)OCH_2O_2\cdot$ with NO produces excited alkoxy radicals, $CH_3C(O)OCH_2O^*\cdot$, which are more prone to decompose to give $CH_3C(O)OH$ than their counterparts produced in the less exothermic peroxy radical self-reaction. Tuazon et al.[15] suggested that α-ester rearrangement proceeds via a five-membered transition state. The five-membered ring is expected to have a ring strain of ≈6 kcal mol^{-1},[15] and α-ester rearrangement will have a substantial activation barrier. Assuming reaction 24 leads to formation of a significant fraction of excited alkoxy radicals $CH_3C(O)OCH_2O^*\cdot$ that possess internal energy exceeding that necessary to overcome the barrier for α-ester rearrangement, the mechanism can be described as follows:



$$CH_3C(O)OCH_2O_2\cdot + NO \rightarrow CH_3C(O)OCH_2O^*\cdot + NO_2 \quad (24)$$

$$CH_3C(O)OCH_2O^*\cdot \rightarrow CH_3C(O)OH + HCO\cdot \quad (25)$$

$$CH_3C(O)OCH_2O^*\cdot + M \rightarrow CH_3C(O)OCH_2O\cdot + M \quad (26)$$

$$CH_3C(O)OCH_2O\cdot + O_2 \rightarrow CH_3C(O)OC(O)H + HO_2 \quad (17)$$

$$CH_3C(O)OCH_2O\cdot \rightarrow CH_3C(O)OH + HCO\cdot \quad (18)$$

Some fraction of the excited alkoxy radicals undergoes prompt α-ester rearrangement via reaction 25; the remainder will lose their energy through collision with a third body M via reaction 26. Similar chemical activation effects have been reported for other alkoxy radicals (e.g., $CF_3CFHO\cdot$,[17] $HOCH_2CH_2O\cdot$,[18] $CH_2ClO\cdot$ [19]). The yield of acetic acid can be expressed as

$$Y(CH_3C(O)OH) = Y(RO\cdot)\left(\frac{1}{\frac{k_{17}}{k_{18}}[O_2] + 1}\right) + Y\cdot \quad (III)$$

where $Y(RO\cdot)$ is the fraction of the alkoxy radicals that becomes thermalized and Y^* is the yield of the alkoxy radicals which undergoes prompt α-ester rearrangement to give $CH_3C(O)OH$. A nonlinear least-squares fit of equation III to the $CH_3C(O)OH$ data in Figure 6 gives $k_{17}/k_{18} = 0.0052 \pm 0.0022$ Torr^{-1}, $Y(RO\cdot) = 0.61 \pm 0.08$, and $Y^* = 0.20 \pm 0.08$. Averaging parameters derived from the two data sets shown in Figure 6 give $Y(RO\cdot) = 0.63 \pm 0.10$. It is gratifying that consistent values of k_{17}/k_{18} are derived from the $CH_3C(O)OH$ and $CH_3C(O)OC(O)H$ data shown in Figures 5 and 6. Averaging the four determinations gives $k_{17}/k_{18} = 0.0054 \pm 0.0022$ Torr^{-1}. In one atmosphere of air ($[O_2] = 160$ Torr) containing NO at 296 K it can be calculated that 65 ± 14% of the $CH_3C(O)OCH_2O\cdot$ radicals undergo α-ester rearrangement while 35 ± 5% react with O_2.

4. Implications for Atmospheric Chemistry

In the atmosphere $CH_3C(O)OCH_3$ can be removed by reaction with OH radicals and Cl atoms, photolysis, and/or wet/dry deposition. The kinetics of the reaction of OH radicals with $CH_3C(O)OCH_3$ have been the subject of three investigations.[1,20,21] The reported rate constants are in good agreement $k_1 = (3.85 \pm 0.16) \times 10^{-13}$ [1], $(3.22 \pm 0.26) \times 10^{-13}$,[20] and $(3.41 \pm 0.29) \times 10^{-13}$ [21] cm^3 molecule^{-1} s^{-1}. Assuming an atmospheric lifetime for methane of 9 years[22] and a rate constant for the CH_4 + OH reaction of 6.3×10^{-15} cm^3 molecule^{-1} s^{-1} leads to an estimate for the atmospheric lifetime of $CH_3C(O)OCH_3$ against reaction with OH of 60 days. As discussed by Notario et al.,[11] for typical atmospheric concentrations of Cl atoms and OH radicals, reaction with Cl atoms is a negligible loss process of $CH_3C(O)OCH_3$ compared to reaction with OH radicals. As discussed by Nriagu,[23] the low Henry's law coefficients of esters ($K_H = 8$ M atm^{-1} for methyl acetate) probably preclude wet deposition from being a significant atmospheric loss mechanism for methyl acetate. Photolysis of methyl acetate is only important below 240 nm[24] and will not be of any significance in the lower atmosphere.

In the present work we have used Cl atoms to initiate oxidation of $CH_3C(O)OCH_3$, whereas in the atmosphere initiation is provided by OH radical attack. There are no available data concerning the relative importance of attack of OH radicals on the two different $-CH_3$ groups in $CH_3C(O)OCH_3$. In the present study we show that the majority of Cl atom reaction occurs at the $-OCH_3$ group. OH radicals are six times less reactive than Cl atoms toward $CH_3C(O)OCH_3$, and it seems reasonable to suppose that OH radicals will be more discriminating than Cl atoms. Structure−reactivity relationships[25] also suggest that the majority (70%) of OH attack will proceed at the $-OCH_3$ group. Hence, we conclude that the reaction with OH gives predominantly the alkyl radical $CH_3C(O)OCH_2\cdot$ which is rapidly converted into the corresponding peroxy radical $CH_3C(O)OCH_2O_2\cdot$. As with other alkyl peroxy radicals, the atmospheric fate of $CH_3C(O)OCH_2O_2\cdot$ radicals will be reaction with either NO, NO_2, HO_2, or other peroxy radicals. Reaction of $CH_3C(O)OCH_2O_2\cdot$ radicals with NO_2 gives a thermally unstable peroxy nitrate which will decompose to regenerate the $CH_3C(O)OCH_2O_2\cdot$ radicals. Reaction of $CH_3C(O)OCH_2O_2\cdot$ radicals with NO produces the alkoxy radical $CH_3C(O)OCH_2O\cdot$. We show here that under atmospheric conditions there are two competing loss processes for $CH_3C(O)OCH_2O\cdot$ radicals; decomposition via α-ester rearrangement to give $CH_3C(O)OH$ and HCO radicals, or reaction with O_2 to give $CH_3C(O)OCHO$. Chemical activation plays an important role in the fate of $CH_3C(O)OCH_2O\cdot$ radicals. A significant fraction, $20/(20 + 61) = 25\%$, of $CH_3C(O)OCH_2O\cdot$ radicals produced in reaction 24a have sufficient internal excitation to undergo prompt decomposition via α-ester rearrangement. The remaining 75% of the $CH_3C(O)OCH_2O\cdot$ radicals are collisionally stabilized and then either react with O_2 or undergo thermal decomposition via α-ester rearrangement. In one atmosphere of air ($[O_2] = 160$ Torr) containing NO at 296 K it can be calculated that 65 ±

14% of the $CH_3C(O)OCH_2O\cdot$ radicals undergo α-ester rearrangement while 35 ± 5% react with O_2.

Acknowledgment. We thank Avedis Mager for his help in the synthesis of $CH_3C(O)OC(O)H$.

References and Notes

(1) Smith, D. F.; McIver, C. D.; Kleindienst, T. E. *Int. J. Chem. Kinet.* **1995**, *27*, 453.

(2) Smith, D. F.; Kleindienst, T. E.; Hudgins, E. E.; McIver, C. D.; Bufalini, J. J. *Int. J. Chem. Kinet.* **1991**, *23*, 907.

(3) Tuazon, E. C.; Carter, W. P. L.; Aschmann, S. M.; Atkinson, R. *Int. J. Chem. Kinet.* **1991**, *23*, 1003.

(4) Wallington, T. J.; Schneider, W. F.; Worsnop, D. R.; Nielsen, O. J.; Sehested, J.; Debruyn, W. J.; Shorter, J. A. *Environ. Sci. Technol.* **1994**, *28*, 320.

(5) Wallington, T. J.; Japar, S. M. *J. Atmos. Chem.* **1989**, *9*, 399.

(6) Schijf, R.; Stevens, W. *Recl. Trav. Chim.* **1966**, *85*, 627.

(7) Crawford, M. A.; Wallington, T. J.; Szente, J. J.; Maricq, M. M.; Francisco, J. S. *J. Phys. Chem. A* **1999**, *103*, 365.

(8) Atkinson, R.; Baulch, D. L.; Cox, R. A.; Hampson, R. F.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **1997**, *26*, 521.

(9) Wallington, T. J.; Hurley, M. D.; Ball, J. C.; Jenkin, M. E. *Chem. Phys. Lett.* **1993**, *211*, 41.

(10) Wine, P. H.; Semmes, D. H. *J. Phys. Chem.* **1983,** *87*, 3572.

(11) Notario, A.; Le Bras, G.; Mellouki, A. *J. Phys. Chem. A* **1998**, *102*, 3112.

(12) Wallington, T. J.; Andino, J. M.; Ball, J. C.; Japar, S. M. *J. Atmos. Chem.* **1990**, *10*, 301.

(13) Olsson, B. E. R.; Hallquist, M.; Ljungstrom, E.; Davidsson, J. *Int. J. Chem. Kinet.* **1997**, *29*, 195.

(14) Wallington, T. J.; Guschin, A.; Hurley, M. D. *Int. J. Chem. Kinet.* **1998**, *30*, 310.

(15) Tuazon, E. C.; Aschmann, S. M.; Atkinson, R.; Carter, W. P. L. *J. Phys. Chem. A* **1998**, *102*, 2316.

(16) Stein, T. N. N.; Christensen, L. K.; Platz, J.; Sehested, J.; Nielsen, O. J.; Wallington, T. J. *J. Phys. Chem. A* **1999**, *103*, 5705.

(17) Wallington, T. J.; Hurley, M. D.; Fracheboud, J. M.; Orlando, J. J.; Tyndall, G. S.; Sehested, J.; Møgelberg, T. E.; Nielsen, O. J. *J. Phys. Chem.* **1996**, *100*, 18116.

(18) Orlando, J. J.; Tyndall, G. S.; Bilde, M.; Ferronato, C.; Wallington, T. J.; Vereecken, L.; Peeters, J. *J. Phys. Chem. A* **1998**, *102*, 8116.

(19) Bilde, M.; Orlando, J. J.; Tyndall, G. S.; Wallington, T. J.; Hurley, M. D.; Kaiser, E. W. *J. Phys. Chem. A* **1999**, *103*, 3963.

(20) El Boudali, A.; Le Calvé, S.; Le Bras, G.; Mellouki, A. *J. Phys. Chem.* **1996**, *30*, 12364.

(21) Wallington, T. J.; Dagaut, P.; Liu, R.; Kurylo, M. J. *Int. J. Chem. Kinet.* **1988**, *20*, 177.

(22) Prinn, R. G.; Weiss, R. F.; Miller, B. R.; Huang, J.; Alyea, F. N.; Cunnold, D. M.; Fraser, P. J.; Hartley, D. E.; Simmonds, P. G. *Science* **1995**, *269*, 187.

(23) Nriagu, J. O. *Advances in Environmental Science and Technology, 24: Gaseous Pollutants*; John Wiley & Sons: New York, 1992.

(24) . Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; John Wiley & Sons: New York, 1966.

(25) Kwok, E. C.; Atkinson, R. *Atmos. Environ.* **1995**, *29*, 1685.