Atmospheric Chemistry of a Model Biodiesel Fuel, CH₃C(O)(CH₂)₂OC(O)CH₃: Kinetics, Mechanisms, and Products of Cl Atom and OH Radical Initiated Oxidation in the Presence and Absence of NOₓ

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Relative rate techniques were used to study the kinetics of the reactions of Cl atoms and OH radicals with ethylene glycol diacetate, CH₃C(O)(CH₂)₂OC(O)CH₃, in 700 Torr of N₂/O₂ diluent at 296 K. The rate constants measured were 
\[ k(\text{Cl} + \text{CH₃C(O)(CH₂)₂OC(O)CH₃}) = (5.7 \pm 1.1) \times 10^{-12} \text{ and } k(\text{OH} + \text{CH₃C(O)(CH₂)₂OC(O)CH₃}) = (2.36 \pm 0.34) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \]

Product studies of the Cl atom initiated oxidation of ethylene glycol diacetate in the absence of NO in 700 Torr of O₂/N₂ diluent at 296 K show the primary products to be \( \text{CH₃C(O)OC(O)CH₂OC(O)CH₃} \), \( \text{CH₃C(O)OC(OH)} \), and \( \text{CH₃C(O)OH} \). Product studies of the Cl atom initiated oxidation of ethylene glycol diacetate in the presence of NO in 700 Torr of O₂/N₂ diluent at 296 K show the primary products to be \( \text{CH₃C(O)OC(OH)CH₃} \) and \( \text{CH₃C(O)OH} \). The CH₃C(O)OC(OH)₂ radical is formed during the Cl atom initiated oxidation of ethylene glycol diacetate in the presence of NO in 700 Torr of O₂/N₂ diluent at 296 K. The CH₃C(O)OC(OH)₂ radical with NO gives chemically activated CH₃C(O)OC(OH)₂ radicals which are more likely to undergo decomposition via the α-ester rearrangement than CH₃C(O)OCH₂O radicals produced in the peroxy radical self-reaction.

1. Introduction

Energy security and climate change concerns have prompted increased interest in alternative transportation fuels derived from biogenic sources.¹⁻³ The principal biofuels under consideration are methyl esters of long chain fatty acids (e.g., CH₃(CH₂)₇-CH=CH(CH₂)₇C(O)OH from oleic acid and CH₃(CH₂)₇C(O)-OCH₃ from palmitic acid) for blending in diesel fuel and alcohols (e.g., C₂H₅OH, C₃H₇OH, and C₄H₉OH) for blending in gasoline. Biodiesel has an energy density which is similar to that of petroleum diesel and so provides similar fuel economy. Biodiesel is made via a relatively simple transesterification process from triglycerides.

During biodiesel production, glycerine (CH₂OHCH(OH)CH₂-OH, propane-1,2,3-triol) is formed in significant quantities as a coproduct. One of the technical hurdles facing the biodiesel industry is finding commercially attractive uses for glycerine. One possible use for this material is to convert it into a compound for blending with diesel fuel. Glycerine is not a viable blending component because of its low solubility in hydrocarbons and high affinity for water. However, glycerine can be transformed into compounds with more suitable blending properties. For example, acylation using acetic acid, propionic acid, or longer chain acids provides molecules which are more soluble in hydrocarbon solvents like diesel fuel and less soluble in water. Prior to the use of such acylated glycerine derivatives, information on their atmospheric chemistry is required. In this study we investigate the atmospheric fate of ethylene glycol diacetate, CH₂C(O)O(CH₂)₂OC(O)CH₃, as a model compound for such acylated glycerine molecules. Ethylene glycol diacetate was chosen as a model because its vapor pressure is greater than, but its chemistry is expected to be similar to, the analogous acylated glycerine derivatives.

2. Experimental Section

The experiments were performed in a 140-L Pyrex reactor interfaced to a Mattson Sirius 100 FTIR spectrometer. The reactor was surrounded by 22 fluorescent blacklamps (GE F15T8-BL) which were used to photochemically initiate the experiments. Chlorine atoms were produced by photolysis of molecular chlorine.

\[ \text{Cl}_2 + h\nu \rightarrow \text{Cl} + \text{Cl} \] (1)
OH radicals were produced by photolysis of CH$_3$ONO in the presence of NO in air.

\[
\text{CH}_3\text{ONO} + h\nu \rightarrow \text{CH}_3\text{O}^+ + \text{NO} \quad (2)
\]

\[
\text{CH}_3\text{O}^+ + \text{O}_2 \rightarrow \text{HO}_2 + \text{HCHO} \quad (3)
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad (4)
\]

Relative rate techniques were used to measure the rate constant of interest relative to a reference reaction whose rate constant has been established previously. The relative rate method is a well-established technique for measuring the reactivity of Cl atoms and OH radicals with organic compounds.$^4$ Kinetic data are derived by monitoring the loss of CH$_3$C(O)O(CH$_2$)$_2$OC(O)CH$_3$ relative to one or more reference compounds. The decays of CH$_3$C(O)O(CH$_2$)$_2$OC(O)CH$_3$ and the reference are then plotted using the expression

\[
\begin{align*}
\ln \left( \frac{[\text{reactant}]}{[\text{reactant}]_0} \right) &= \frac{k_{\text{reactant}}}{k_{\text{reference}}} \times \ln \left( \frac{[\text{reference}]}{[\text{reference}]_0} \right) \quad (1)
\end{align*}
\]

where $[\text{reactant}]_0$, $[\text{reactant}]$, $[\text{reference}]_0$, and $[\text{reference}]$ are the concentrations of CH$_3$C(O)O(CH$_2$)$_2$OC(O)CH$_3$ and the reference compound at times "0" and "r", and $k_{\text{reactant}}$ and $k_{\text{reference}}$ are the rate constants for reactions of Cl atoms or OH radicals with the CH$_3$C(O)O(CH$_2$)$_2$OC(O)CH$_3$ and the reference compound. Plots of $\ln([\text{reactant}]/[\text{reactant}]_0$ versus $\ln([\text{reference}]_0/[\text{reference}]$) should be linear, pass through the origin, and have a slope of $k_{\text{reactant}}/k_{\text{reference}}$.

CH$_3$ONO was synthesized by the dropwise addition of concentrated sulfuric acid to a saturated solution of NaNO$_2$ in methanol.$^5$ Acetoxyacetic acid anhydride, CH$_3$C(O)O(CH$_2$)$_2$OC(O)CH$_3$, was prepared from acetoxyacetyl chloride (Aldrich) and sodium acetate in tetrahydrofuran as described by Schijf and Stevens.$^6$ Acetoxyacetic acid anhydride was purified by repeated bulb-to-bulb vacuum transfers. The sample of acetoxyacetic acid anhydride contained acetic anhydride which could not be removed, possibly due to the formation of an azeotropic mixture. The presence of the acetic anhydride impurity, together with the low vapor pressure of acetoxyacetic acid anhydride, prevented an absolute calibration of the acetoxyacetic anhydride reference spectrum. Other reagents were obtained from commercial sources. Experiments were conducted in 700 Torr total pressure of O$_2$/N$_2$ diluent at 296 ± 1 K. Concentrations of reactants and products were monitored by FTIR spectroscopy. IR spectra were derived from 32 coadded interferograms with a spectral resolution of 0.25 cm$^{-1}$ and an analytical path length of 27 m.

In smog chamber experiments it is important to check for the unwanted loss of reactants and products via photolysis, dark chemistry, and heterogeneous reactions. Control experiments were performed in which (i) mixtures of reactants (except Cl$_2$) were subjected to UV irradiation for 10–20 min and (ii) product mixtures obtained after the UV irradiation of reactant mixtures were allowed to stand in the dark in the chamber for 20 min. There was no observable loss of reactants or products, suggesting that photolysis, dark chemistry, and heterogeneous reactions are not significant complications in the present work. Unless stated otherwise, quoted uncertainties are two standard deviations from least-squares regressions.

3. Results

3.1. Relative Rate Study of $k$(Cl + CH$_3$C(O)O(CH$_2$)$_2$OC(O)CH$_3$). The kinetics of reaction 5 were measured relative to those of reactions 6 and 7:

\[
\text{Cl} + \text{CH}_3\text{C}(\text{O})(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3 \rightarrow \text{products} \quad (5)
\]

\[
\text{Cl} + \text{CH}_3\text{Cl} \rightarrow \text{products} \quad (6)
\]

\[
\text{Cl} + \text{C}_2\text{H}_5\text{Cl} \rightarrow \text{products} \quad (7)
\]

Reaction mixtures consisted of 1.9–2.6 mTorr of CH$_3$C(O)O(CH$_2$)$_2$OC(O)CH$_3$, 88–103 mTorr Cl$_2$, and 14.7–30.1 mTorr of either C$_2$H$_5$Cl or CH$_3$Cl in a total of 700 Torr air or N$_2$. The observed loss of CH$_3$C(O)O(CH$_2$)$_2$OC(O)CH$_3$ versus those of the reference compounds is plotted in Figure 1. Linear least-squares analysis of the data in Figure 1 gives $k_5/k_6 = 10.9 \pm 1.1$ and $k_5/k_7 = 0.77 \pm 0.08$. Using $k_6 = 4.8 \times 10^{-13}$ and $k_7 = 8.04 \times 10^{-12}$ gives $k_5 = (5.2 \pm 0.5) \times 10^{-12}$ and $(6.2 \pm 0.6) \times 10^{-13}$ cm$^3$ molecule$^{-1}$ s$^{-1}$. Indistinguishable values of $k_5$ are obtained using the two different references. We choose
to cite a final value which is the average of the individual determinations together with error limits which encompass the extremes of the determinations; therefore, \( k_s = (5.7 \pm 1.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \).

3.2. Relative Rate Study of \( k(\text{OH} + \text{CH}_3\text{C}(\text{O})(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3) \). The kinetics of reaction 8 were measured relative to reactions 9 and 10:

\[
\begin{align*}
\text{OH} + \text{CH}_3\text{C}(\text{O})(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3 & \rightarrow \text{products} \quad (8) \\
\text{OH} + \text{C}_2\text{H}_4 & \rightarrow \text{products} \quad (9) \\
\text{OH} + \text{C}_2\text{H}_2 & \rightarrow \text{products} \quad (10)
\end{align*}
\]

Initial reaction mixtures consisted of 1.8–2.5 mTorr of \( \text{CH}_3\text{C}(\text{O})(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3 \), 0–19 mTorr of \( \text{NO} \), 95–102 mTorr \( \text{CH}_3\text{NO} \), and 7.2–11.5 mTorr of either \( \text{C}_2\text{H}_4 \) or \( \text{C}_2\text{H}_2 \) in 700 Torr total pressure of air dilluent. Figure 2 shows the loss of \( \text{CH}_3\text{C}(\text{O})(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3 \) plotted versus loss of the reference compounds. Linear least-squares analysis gives \( k_9/k_8 = 0.28 \pm 0.03 \) and \( k_9/k_{10} = 2.7 \pm 0.3 \). Using \( k_9 = 8.7 \times 10^{-12} \) and \( k_{10} = 8.45 \times 10^{-13} \) we derive \( k_8 = (2.44 \pm 0.26) \times 10^{-12} \) and \( (2.28 \pm 0.26) \times 10^{-12} \). Indistinguishable values of \( k_8 \) are obtained using the two different references. We choose to cite a final value which is the average of the individual determinations together with error limits which encompass the extremes of the determinations; therefore, \( k_8 = (2.36 \pm 0.34) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). While there have been no previous measurements of \( k_8 \), O’Donnell et al.\(^{11}\) have reported rate coefficients for reactions of \( \text{OH} \) radicals with a series of related alkoxy esters. They report \( k(\text{OH} + \text{CH}_3\text{C}(\text{O})(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3) = (7.83 \pm 0.31) \times 10^{-12} \) and \( k(\text{OH} + \text{CH}_3\text{C}(\text{O})(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3) = (1.21 \pm 0.29) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \) at 298 K. Consistent with the available data concerning the reactivity of ethers and esters, \( \text{CH}_3\text{C}(\text{O})(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3 \) is approximately 3 times less reactive than \( \text{CH}_3\text{C}(\text{O})(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3 \) reflecting the fact that \( -\text{OCH}_3 \) is more activating than the \( -\text{OC}(\text{O})\text{CH}_3 \) group.

3.3. Structure–Activity Relationships. The kinetic results can be compared with the rate coefficients predicted using the structure–activity relationship (SAR) approach developed by Atkinson and co-workers.\(^ {12,14} \) The SAR method provides a means of calculating the rate of reaction of the \( \text{OH} \) radical with a large number of organic compounds. Calculation of the H-atom abstraction rate from \( \text{C}^\text{–H} \) bonds is based on the estimated \( -\text{CH}_3, -\text{CH}_2-, \) and \( -\text{CH}– \) group rate constants, where the group rate constant is influenced by the nature of the \( \alpha \) substituent groups. Agreement with experimental values is generally good, except in cases where long-range effects require consideration of \( \beta \) substituent groups. Using the group rate constants and substituent factors recommended by Kwok and Atkinson,\(^ {13} \) the rate constant for reaction 8 is calculated to be \( k_8(\text{SAR}) = 3.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). Mellouki et al.\(^ {15} \) reviewed the kinetics and mechanisms of the oxidation of oxygenated organic compounds and have proposed group rate constants for ester \( \text{CH}_x \) (\( x = 1,2,3 \)) groups that depend on whether the \( \text{CH}_x \) group is on the acyl or alkoxy group of the ester and whether the \( \text{CH}_x \) group is in the \( \alpha, \beta, \gamma, \) or \( \delta \) position. Using the appropriate group rate constants, this approach gives a value of \( k_8 = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \). Using the group rate constants from Mellouki et al.\(^ {15} \) we conclude that 7% of \( \text{OH} \) atom attack occurs at the terminal \( -\text{CH}_3 \) group, while 93% of \( \text{OH} \) atom attack occurs at the bridging \( -\text{CH}_2- \) groups. Mellouki et al.\(^ {15} \) also discuss the reactivity of bridging \( -\text{CH}_2- \) groups in difunctional oxygenated compounds. They cite examples where the reactivity of the bridging \( -\text{CH}_2- \) groups is the same as expected from \( \alpha \) substituents and examples where
the reactivity is enhanced, suggesting the effect of long-range activation. The experimental value determined in this work, $k_8 = (2.36 \pm 0.34) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, is consistent with the SAR estimates of both Kwok and Atkinson\textsuperscript{13} and Mellouki et al.\textsuperscript{15} Finally, Notario et al.\textsuperscript{16} extended the SAR approach to the reaction of Cl atoms with a series of esters. Using the modified SAR approach of Notario et al.\textsuperscript{16} gives $k_5 = (5.7 \pm 1.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is consistent with the experimental value determined in this work, $k_5 = (5.7 \pm 1.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

3.4. Products of the Cl Atom Initiated Oxidation of CH\textsubscript{3}C-(O)(CH\textsubscript{2})\textsubscript{2}OC(O)CH\textsubscript{3} in the Absence of NO. The Cl atom initiated oxidation of ethylene glycol diacetate in the absence of NO was investigated by irradiating mixtures containing 2–5 mTorr CH\textsubscript{3}C(O)(CH\textsubscript{2})\textsubscript{2}OC(O)CH\textsubscript{3} and 86–100 mTorr Cl\textsubscript{2} in 700 Torr of O\textsubscript{2}/N\textsubscript{2} diluent. Reaction mixtures were subjected to 5–7 successive irradiations of 5–30 s duration. Figure 3 shows spectra acquired before (A) and after (B) a 15 s irradiation of 4.1 mTorr CH\textsubscript{3}C(O)(CH\textsubscript{2})\textsubscript{2}OC(O)CH\textsubscript{3} and 91.7 mTorr Cl\textsubscript{2} in 700 Torr of air. The consumption of CH\textsubscript{3}C(O)(CH\textsubscript{2})\textsubscript{2}OC(O)CH\textsubscript{3} was 41%. Panel (C) shows the product spectrum obtained by subtracting CH\textsubscript{3}C(O)CH\textsubscript{2}CH\textsubscript{2}OCH\textsubscript{3} features from panel B. Comparison of panel (C) with the reference spectrum in panel D shows that acetic formic anhydride, CH\textsubscript{3}C(O)OC(O)CH\textsubscript{2}OH, is an important product. Panel (E) shows the result of subtracting CH\textsubscript{3}C(O)OC(O)CH\textsubscript{2}OH features from panel C. Comparison of panel (E) with the reference spectrum in panel F shows that acetic acid, CH\textsubscript{3}C(O)OH, is a product. Panel (G) is the result of subtracting CH\textsubscript{3}C(O)OH features from panel E. Comparison of panel (G) with the reference spectrum in panel H shows that CH\textsubscript{3}C(O)OC(O)CH\textsubscript{2}OC(O)CH\textsubscript{3} is a product. Figure 4 shows the formation of products versus the loss of CH\textsubscript{3}C(O)(CH\textsubscript{2})\textsubscript{2}OC(O)CH\textsubscript{3} for experiments in the presence of either 5 or 700 Torr of O\textsubscript{2} at 700 Torr total pressure made up with N\textsubscript{2} as appropriate. The linearity of the data suggests that secondary loss or formation of these products is not important under these conditions. The yields of CH\textsubscript{3}C(O)-OC(O)H and CH\textsubscript{3}C(O)OH clearly depend on the O\textsubscript{2} concentration, while the yield of CH\textsubscript{3}C(O)OC(O)CH\textsubscript{2}OC(O)CH\textsubscript{3} is independent of O\textsubscript{2} concentration.

A diagram of the reaction pathways for the Cl atom initiated oxidation of ethylene glycol diacetate in the absence of NO is given in Figure 5. Reaction of CH\textsubscript{3}C(O)OCH\textsubscript{2}CH\textsubscript{2}OC(O)CH\textsubscript{3} with Cl atoms can occur via two channels.

\begin{equation}
\text{CH}_3\text{C(O)OCH}_2\text{CH}_2\text{OC(O)CH}_3 + \text{Cl} \rightarrow \text{CH}_3\text{C(O)OC(H)CH}_2\text{OC(O)CH}_3 + \text{HCl} \quad (11a)
\end{equation}

\begin{equation}
\text{CH}_3\text{C(O)OCH}_2\text{CH}_2\text{OC(O)CH}_3 + \text{Cl} \rightarrow \cdot\text{CH}_2\text{C(O)OCH}_2\text{CH}_2\text{OC(O)CH}_3 + \text{HCl} \quad (11b)
\end{equation}

We have no direct measure of the relative importance of the two channels; however, in studies of the Cl and OH initiated oxidation of acetates,\textsuperscript{17–20} H atom abstraction from the CH\textsubscript{3}C-(O) group was found to be of minor importance. Reaction 11a is expected to be the dominant channel, and the observed products are consistent with this assumption. Reaction 11a followed by reaction with O\textsubscript{2} results in the formation of alkyl peroxy radicals.

\begin{equation}
\text{CH}_3\text{C(O)OC(H)CH}_2\text{OC(O)CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)OCHOO(H)CH}_2\text{OC(O)CH}_3 \quad (12)
\end{equation}
In the absence of NO, reaction of CH$_3$C(O)OCHO$_2$OCH$_2$OCH$_3$ with other peroxy radicals results in the formation of alkoxy radicals

$$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{OCH}_2\text{OC}(\text{O})\text{CH}_3 + \text{ROO}^\bullet \rightarrow \text{CH}_3\text{C}(\text{O})\text{CHO}\text{CH}_2\text{OC}(\text{O})\text{CH}_3 + \text{RO}^\bullet + \text{O}_2 \text{ (13)}$$

Self-reaction of CH$_3$C(O)OCHO$_2$OCH$_2$OC(O)CH$_3$ radicals to give molecular products is also a possibility.

$$2\text{CH}_3\text{C}(\text{O})\text{OCHO}_2\text{OC}(\text{O})\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{CH}_2\text{OC}(\text{O})\text{CH}_3 + \text{CH}_3\text{C}(\text{O})\text{OCHOHCH}_2\text{OC}(\text{O})\text{CH}_3 \text{ (14)}$$

The alkoxy radicals formed in reaction 13 can react with O$_2$ to form acetoxyacetic acetic anhydride and HO$_2$.

$$\text{CH}_3\text{C}(\text{O})\text{OCHO}\text{CH}_2\text{OC}(\text{O})\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{CH}_2\text{OC}(\text{O})\text{CH}_3 + \text{HO}_2 \text{ (15)}$$

Tuazon et al.\textsuperscript{17} first reported, and others\textsuperscript{18-20} have confirmed, that alkoxy radicals of the form RC(O)OCHO$^+$ can undergo a rapid rearrangement and decomposition (α-ester rearrangement) to form RC(O)OH and R′CO$^\bullet$.

$$\text{CH}_3\text{C}(\text{O})\text{OCHO}\text{CH}_2\text{OC}(\text{O})\text{CH}_3 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OH} + \text{OCCH}_2\text{OC}(\text{O})\text{CH}_3 \text{ (16)}$$

The fate of CH$_3$C(O)OC•H$_2$ is discussed in detail in a paper on the atmospheric oxidation mechanism of methyl acetate by Christensen et al.\textsuperscript{18} It was concluded that CH$_3$C(O)OC•H$_2$ radicals add O$_2$ and then react with other RO$_2$• radicals to form CH$_3$C(O)OCH$_2$O• radicals.

$$\text{CH}_3\text{C}(\text{O})\text{OC•H}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{CH}_2\text{OO•} \text{ (18)}$$

$$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{OO•} + \text{RO}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{O•} \text{ (19)}$$

There are two competing loss mechanisms for CH$_3$C(O)-OCH$_2$O• radicals: reaction with O$_2$ and α-ester rearrangement.

$$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{O•} + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H} + \text{HO}_2\text{•} \text{ (20)}$$

$$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{O•} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OH} + \text{HCO•} \text{ (21)}$$

Yields of CH$_3$C(O)OC(O)H and CH$_3$C(O)OH observed from the Cl initiated oxidation of CH$_3$C(O)OCH$_2$H$_2$OC(O)CH$_3$ in the absence of NO are shown in Figure 6 as a function of [O$_2$]. The yield of CH$_3$C(O)OC(O)H increases, while the yield of CH$_3$C(O)OH decreases with increasing oxygen concentration. The yield of CH$_3$C(O)OC(O)CH$_2$OC(O)CH$_3$ is independent of oxygen concentration. The simplest explanation for these results is that CH$_3$C(O)OC(O)CH$_2$OC(O)CH$_3$ reacts with Cl in the presence of O$_2$ to form the alkyl peroxy radicals CH$_3$C(O)-OCHO$^+$CH$_2$OC(O)CH$_3$, via reactions 11a and 12. The yield of CH$_3$C(O)OC(O)CH$_2$OC(O)CH$_3$ is independent of O$_2$ concentration, suggesting that reaction 15 is either very important or not very important for all $[O_2]$ studied, depending on the rate constant ratio, $k_{15}/k_{17}$. The fact that we observe significant amounts of CH$_3$C(O)OC(O)H and CH$_3$C(O)OH suggests that reaction 15 is not very important. The independence of the CH$_3$C(O)OC(O)CH$_2$OC(O)CH$_3$ yields on $[O_2]$ is consistent with the molecular channel of the self-reaction, reaction 14, being responsible for the anhydride formation. The molecular channel of the self-reaction of CH$_3$C(O)OCHO$^+$CH$_2$OC(O)CH$_3$ radicals, reaction 14, produces an alcohol, CH$_3$C(O)OCHOHCH$_2$OC(O)CH$_3$, along with acetoxyacetic acetic anhydride. While there are residual features in the product spectrum when the IR features of the identified products are subtracted, there are no features that are characteristic of an alcohol, such as an OH feature at 3600–3800 cm$^{-1}$. It is possible that this feature is weak: however, it is also possible that the alcohol is reactive and is quickly consumed by reaction with Cl atoms. The remaining CH$_3$C(O)OCHO$^+$CH$_2$OC(O)CH$_3$ radicals react with RO$_2$ to give alkoxy radicals, CH$_3$C(O)CHO$^+$CH$_2$OC(O)CH$_3$. As seen in Figure 6, the yield of CH$_3$C(O)OH is small at high $[O_2]$, suggesting that α-ester rearrangement of CH$_3$C(O)-OCHO$^+$CH$_2$OC(O)CH$_3$, reaction 16, is not very important. The alkoxy radical decomposes to form CH$_3$C(O)OC(O)H and •CH$_2$OC(O)CH$_3$, reaction 17. The alkyl peroxy radical, CH$_3$C(O)OC(O)OO•, is formed via reaction 18. Of the CH$_3$C(O)OCH$_2$OO• radicals formed, some will react to form CH$_3$C(O)OC(O)H via channels that are independent of O$_2$ concentration, reactions 22 and 23, while the balance will react with RO$_2$ to form CH$_3$C(O)-OCH$_2$OO• radicals, reaction 19. The fate of CH$_3$C(O)OCH$_2$O• radicals is either reaction with O$_2$ or α-ester rearrangement, reactions 20 and 21.

$$2\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{OO•} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H} + \text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{OH} + \text{O}_2 \text{ (22)}$$

$$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{OO•} + \text{HO}_2\text{•} \rightarrow \text{CH}_3\text{O}(\text{O})\text{OC}(\text{O})\text{H} + \text{H}_2\text{O} + \text{O}_2 \text{ (23)}$$

Christensen et al.\textsuperscript{18} showed that, in the Cl atom initiated oxidation of methyl acetate, the dependence of the CH$_3$C(O)-OC(O)H and CH$_3$C(O)OH yields on $[O_2]$ can be expressed in terms of the rate constant ratio $k_{39}/k_{21}$. The yields of CH$_3$C(O)-
OC(O)H and CH$_3$C(O)OH are given by

$$Y(\text{ROY}) = \frac{Y(\text{RO})}{k_{20} k_{21}} [\text{O}_2] + A$$  \hspace{1cm} (II)

$$Y(\text{CH}_3\text{C(O)OH}) = \frac{Y(\text{RO})}{k_{20} k_{21}} [\text{O}_2] + B$$  \hspace{1cm} (III)

where $Y(\text{RO})$ is the yield of the CH$_3$C(O)OCH$_2$O• radical. The terms $A$ and $B$ in the equations are required to account for the formation of CH$_3$C(O)OC(O)H and CH$_3$C(O)OH via channels that are independent of O$_2$ concentration. Christensen et al.\(^{18}\) fit eqs II and III to their product data in the absence of NO and determined $k_{20}/k_{21} = 0.0054 \pm 0.0022$ Torr$^{-1}$. The curves in Figure 6 are least-squares fits of expressions II and III to the data using $k_{20}/k_{21} = 0.0054 \pm 0.0022$ Torr$^{-1}$. From the CH$_3$C(O)OC(O)H data in Figure 6 we derive $Y(\text{RO}) = 0.58 \pm 0.06$ and $A = 0.81 \pm 0.04$. From the CH$_3$C(O)OH data in Figure 6 we derive $Y(\text{RO}) = 0.53 \pm 0.10$ and $B = 0.03 \pm 0.03$. The values of $Y(\text{RO})$ derived from the CH$_3$C(O)OC(O)H and CH$_3$C(O)OH yields are consistent. Averaging the two determinations of $Y(\text{RO})$ together with uncertainties that encompass the individual measurements gives $Y(\text{RO}) = 0.55 \pm 0.12$. The yield of CH$_3$C(O)OH from O$_2$ independent channels is effectively zero. These parameters can be used to determine the yield of the CH$_3$C(O)OCHO•CH$_2$OC(O)CH$_3$ radicals, $Y(\text{RO})$, in the absence of NO. If decomposition is the sole fate of CH$_3$C(O)OCHO•CH$_2$OC(O)CH$_3$ radicals and $\beta$ is the fraction of CH$_3$C(O)OCHO• radicals that react to form CH$_3$C(O)OC(O)H via channels that are independent of O$_2$ concentration, then the following equations apply.

$$Y(\text{RO}) + (\beta \times Y(\text{RO})) = 0.81 \pm 0.04$$  \hspace{1cm} (IV)

$$Y(\text{RO}) - (\beta \times Y(\text{RO})) = 0.55 \pm 0.12$$  \hspace{1cm} (V)

Solving these equations gives $Y(\text{RO}) = 0.68 \pm 0.06$ and $\beta = 0.19 \pm 0.11$. As discussed previously, the acetoxyacetic acid anhydride reference spectrum used in this work is uncalibrated; however, the results presented here, together with carbon balance considerations, suggest that $Y(\text{CH}_3\text{C(O)OC(O)CH}_3) \leq 0.16$ and $Y(\text{CH}_3\text{C(O)OCHOCH}_2\text{OC(O)CH}_3) \leq 0.16$ due to the molecular channel of the CH$_3$C(O)OCHO•CH$_2$OC(O)CH$_3$ radical self-reaction, reaction 14. In this mechanistic analysis we have assumed no contribution from the attack of Cl atoms on the terminal –CH$_3$ groups. If attack occurs on the terminal –CH$_3$ groups, it is conceivable that a series of oxidations, followed by decomposition, would lead to formation of the CH$_3$C(O)OC(O)CH$_3$ radical. However, if this channel was significant, the values of $Y(\text{RO})$ derived from fits of eqs II and III would not be in agreement.

Mauer et al.\(^{21}\) investigated the Cl atom initiated oxidation of ethylene glycol diformate, HC(O)O(CH$_2$)$_2$OC(O)H, in the absence of NO. They found that the alkoxy radical, HC(O)OCHO•CH$_2$OC(O)H, decomposes to form formic acid anhydride, HC(O)OC(O)H, and *CH$_2$OC(O)H. The fate of *CH$_2$-
OC(O)H is a competition between reaction with O to form
HC(O)OC(O)H and α-ester rearrangement to form HC(O)OH
and HC(O). In the absence of NOx, the formic acid anhydride
and formic acids were 144 ± 29 mol % and 39 ± 8 mol %,
respectively.

3.5. Products of the Cl Atom Initiated Oxidation of CH3C-
(O)OC(CH2)2OC(O)CH3 in the Presence of NO. The Cl atom
initiated oxidation of ethylene glycol diacetate in the
presence of NO was investigated by irradiating mixtures containing 3.3–
7.0 mTorr CH3C(O)OC(CH2)2OC(O)CH3, 24–26 mTorr NO, and
88–100 mTorr Cl2. The experiments were performed at a
constant total pressure of 700 Torr O2/N2 diluent with the O2
partial pressure varied over the range 50–650 Torr. Reaction
mixtures were subjected to 4–12 successive irradiations of
5–120 s duration. A diagram of the reaction pathways for the
Cl atom initiated oxidation of ethylene glycol diacetate in the
presence of NOx is given in Figure 7. In the presence of NO,
CH3C(O)OCH2OC(O)CH3 radicals are formed by reactions
11a and 12, followed by reaction 24.

\[
\text{CH}_3\text{C(O)OC}(\text{CH}_2\text{O})\text{OC(O)CH}_3 \rightarrow \text{CH}_3\text{C(O)OC(O)CH}_3 + \text{NO} \quad (24)
\]

In the presence of NOx, nitrates and nitrates may be formed
through the following reactions

\[
\begin{align*}
\text{CH}_3\text{C(O)OC}(\text{CH}_2\text{O})\text{OC(O)CH}_3 + \text{NO} & \rightarrow \text{CH}_3\text{C(O)OC}(\text{NO})\text{OC(O)CH}_3 \quad (25) \\
\text{CH}_3\text{C(O)OC}(\text{CH}_2\text{O})\text{OC(O)CH}_3 + \text{NO} & \rightarrow \text{CH}_3\text{C(O)OC}(\text{ONO})\text{OC(O)CH}_3 \quad (26) \\
\text{CH}_3\text{C(O)OC}(\text{CH}_2\text{O})\text{OC(O)CH}_3 + \text{NO} & \rightarrow \text{CH}_3\text{C(O)OC}(\text{NO})\text{OC(O)CH}_3 \quad (27)
\end{align*}
\]

Consistent with the fact that the reactions of oxygenated
peroxy radicals with NO generally produce rather small yields
of organic nitrates, there was no evidence in the IR spectra
for the formation of nitrates. The formation of nitrites and
nitrates via reactions 26 and 27 in the present experiments was
suppressed by keeping [NO]/[O2] < 5 × 10^{-4}. In all experiments
CH3C(O)OC(O)H and CH3C(O)OH were identified and quanti-
tied using calibrated reference spectra. Figure 8 shows the
observed yields of the products versus the O2 concentration.
The presence of NO is expected to suppress the self-reaction
of CH3C(O)OC(O)H and CH3C(O)OH, and, in fact,
formation of CH3C(O)OC(O)CH2OC(O)CH3 was not observed.
As in the absence of NO, the yield of CH3C(O)OC(O)H
increased with increasing O2 concentration, while the yield of
CH3C(O)OH decreased.

As discussed in the previous section, CH3C(O)OCHO\text{CH2}-
OC(O)CH3 radicals formed in reaction 24 will decompose via
C–C bond cleavage

\[
\text{CH}_3\text{C(O)OC}(\text{CH}_2\text{O})\text{OC(O)CH}_3 \rightarrow \text{CH}_3\text{C(O)OC(O)H} + \text{CH}_2\text{OC(O)CH}_3 \quad (17)
\]

The CH3OC(O)CH3 radicals will add O2 to give the corresponding
peroxy radicals.

\[
\text{CH}_3\text{C(O)OC}(\text{CH}_2\text{O})\text{OC(O)H}_2 \! + \! O_2 \rightarrow \text{CH}_3\text{C(O)OC}(\text{CH}_2\text{O})\text{OC(O)H}_2 \! + \! \text{HO}_2 \quad (18)
\]

Christensen et al.\textsuperscript{18} observed that the reaction of CH3C(O)-
OCH2OO• with NO, reaction 28, produces excited alkoxy
radicals, CH3C(O)OCH3O•, which either decompose via reaction
29 or lose their excess internal energy through collision
with a third body, reaction 30. The thermalized CH3C(O)-
OCH2OO• radicals formed in reaction 30 either react with O2,
reaction 20, or undergo α-ester rearrangement, reaction 21.

\[
\begin{align*}
\text{CH}_3\text{C(O)OC(O)H}_2\text{O} & \rightarrow \text{CH}_3\text{C(O)OC(O)H}_2\text{O}_2 + \text{NO} \quad (28) \\
\text{CH}_3\text{C(O)OC(O)H}_2\text{O}_2 & \rightarrow \text{CH}_3\text{C(O)OC(O)H}_2\text{O} + \text{HCO} \quad (29) \\
\text{CH}_3\text{C(O)OC(O)H}_2\text{O} + \text{O}_2 & \rightarrow \text{CH}_3\text{C(O)OC(O)H}_2\text{O} + \text{HO}_2 \quad (30) \\
\text{CH}_3\text{C(O)OC(O)H}_2\text{O} & \rightarrow \text{CH}_3\text{C(O)OC(O)H}_2\text{O} + \text{HCO} \quad (21)
\end{align*}
\]

The curves in Figure 8 are least-squares fits of expressions
II and III to the data using k29/k21 = 0.0054 ± 0.0002 Torr\textsuperscript{-1}.
From the CH3C(O)OC(O)H data in Figure 8 we derive Y'(RO•) = 0.80 ± 0.20 and \lambda = 0.84 ± 0.11. From the CH3C(O)OH data in Figure 8 we derive Y'(RO•) = 0.58 ± 0.06 and B = 0.13 ± 0.03. Averaging the two determinations of Y'(RO•) together with uncertainties that encompass the individual measurements, Y'(RO•) = 0.69 ± 0.30. These parameters can be used to determine the yield of CH3C(O)OC(O)H2OC(O)H2 radicals, Y(RO•), in the presence of NO. If decomposition is the sole fate of CH3C(O)OC(O)H2OC(O)H2 radicals, β is
the fraction of CH3C(O)OC(O)H2OO• radicals that react to form
CH3C(O)OC(O)H2 radicals via channels that are independent
of O2 concentration and γ is the fraction of CH3C(O)OC(O)H2OO•
radicals that undergo prompt α-ester rearrangement, then the following
equations apply

\[
Y(RO•) + \left(\beta \times Y(RO•)\right) = 0.84 \pm 0.11 \quad (VI)
\]

\[
Y(RO•) - \left(\beta \times Y(RO•)\right) - \left(\gamma \times Y(RO•)\right) = 0.69 \pm 0.30 \quad (VII)
\]
\[ \gamma \times Y(\text{RO}_x) = 0.13 \pm 0.03 \quad \text{(VIII)} \]

Solving these equations gives \( Y(\text{RO}_x) = 0.83 \pm 0.16, \beta = 0.02 \pm 0.02, \) and \( \gamma = 0.16 \pm 0.05. \) Christensen et al.\(^18\) determined that, in the presence of NO, the fraction of CH\(_3\)C(O)OCH\(_2\)OC(O)H via processes that are not dependent on the O\(_2\) concentration was 0.04 \pm 0.04 and that the yield of alkoxy radicals which undergo prompt rearrangement to form CH\(_3\)C(O)OH is 0.20 \pm 0.08. The fit of the curves to the data in Figure 8 demonstrate that the fate of the CH\(_3\)C(O)OCH\(_2\)OC(O)H radical formed during the Cl initiated oxidation of ethylene glycol diacetate in the presence of NO is consistent with the fate of the CH\(_3\)C(O)OCH\(_2\)OC(O)H radical determined by Christensen et al.\(^18\) in the Cl initiated oxidation of methyl acetate in the presence of NO.

Mauer et al.\(^21\) investigated the Cl atom initiated oxidation of ethylene glycol diformate, HC(O)O(CH\(_2\))\(_2\)OC(O)H, in the presence of NO\(_x\). They found that the alkoxy radical, HC(O)-OCHO(•)CH\(_2\)OC(O)H, decomposes to form formic acid anhydride, HC(O)OC(O)H and •CH\(_2\)OC(O)H. The fate of •CH\(_2\)OC(O)-H is reaction with O\(_2\) to form HCOOC(O)H and α-ester rearrangement to form HCO(OH)H and HC•(O). In the presence of NO\(_x\), the molar yields of formic acid anhydride and formic acid were 173 \pm 34% and 45 \pm 9%, respectively. Evidence was also found for a chemically activated alkoxy radical effect.

4. Implications for Atmospheric Chemistry. The present work improves our understanding of the atmospheric chemistry of ethylene glycol diacetate, CH\(_3\)C(O)(CH\(_2\))\(_2\)OC(O)CH\(_3\). Cl atoms and OH radicals react with CH\(_3\)C(O)(CH\(_2\))\(_2\)OC(O)CH\(_3\) with rate constants of (5.7 \pm 1.1) \times 10^{-12} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}, respectively. The value of \( k(\text{OH} + \text{CH}_3\text{C}(\text{O})(\text{CH}_2)_2\text{OC}(\text{O})\text{CH}_3) \) can be used to provide an estimate of the atmospheric lifetime of CH\(_3\)C(O)(CH\(_2\))\(_2\)OC(O)CH\(_3\). Using a global weighted-average OH concentration of 1.0 \times 10^6 \text{ mole cm}^{-3} \text{ day}^{-1} leads to an estimated lifetime of CH\(_3\)C(O)(CH\(_2\))\(_2\)OC(O)CH\(_3\) with respect to reaction with OH radicals of 4.9 days. The approximate nature of this atmospheric lifetime estimate should be stressed; the average daily concentration of OH radicals in the atmosphere varies significantly with both location and season. The value above is an estimate of the global average lifetime; local lifetime may be different. The major atmospheric oxidation products of ethylene glycol diacetate (CH\(_3\)C(O)(CH\(_2\))\(_2\)OC(O)CH\(_3\), CH\(_3\)C(O)(CH\(_2\))\(_2\)OC(O)H, and CH\(_3\)C(O)OH) are oxygenated organic compounds which are expected to be relatively unreactive toward further gas-phase oxidation reactions.\(^25\) We conclude that ethylene glycol diacetate has a modest kinetic reactivity and a low mechanistic reactivity and appears likely to have a low photochemical ozone creation potential.

Modeling studies are required to provide a precise quantification of the photochemical ozone creation potential but are beyond the scope of the present work.

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References and Notes

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