# The Atmospheric Oxidation of Ethyl Formate and Ethyl Acetate over a Range of Temperatures and Oxygen Partial Pressures

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> ABSTRACT: The Cl-atom-initiated oxidation of two esters, ethyl formate [HC(O)OCH<sub>2</sub>CH<sub>3</sub>] and ethyl acetate [CH<sub>3</sub>C(O)OCH<sub>2</sub>CH<sub>3</sub>], has been studied at pressures close to 1 atm as a function of temperature (249–325 K) and O<sub>2</sub> partial pressure (50–700 Torr), using an environmental chamber technique. In both cases, Cl-atom attack at the CH<sub>2</sub> group is most important, leading in part to the formation of radicals of the type RC(O)OCH(O<sup>•</sup>)CH<sub>3</sub> [R = H, CH<sub>3</sub>]. The atmospheric fate of these radicals involves competition between reaction with O<sub>2</sub> to produce an anhydride compound, RC(O)OC(O)CH<sub>3</sub>, and the so-called  $\alpha$ -ester rearrangement that produces an organic acid, RC(O)OH, and an acetyl radical, CH<sub>3</sub>C(O). For both species studied, the  $\alpha$ -ester rearrangement is found to dominate in air at 1 atm and 298 K. Barriers to the rearrangement of 7.7  $\pm$  1.5 and 8.4  $\pm$  1.5 kcal/mole are estimated for CH<sub>3</sub>C(O)OCH(O<sup>•</sup>)CH<sub>3</sub> and HC(O)OCH(O<sup>•</sup>)CH<sub>3</sub>, respectively, leading to increased occurrence of the O<sub>2</sub> reaction at reduced temperature. The data are combined with those obtained from similar studies of other simple esters to provide a correlation between the rate of occurrence of the  $\alpha$ -ester rearrangement and the structure of the reacting radical. © 2010 Wiley Periodicals, Inc. Int J Chem Kinet 42: 397–413, 2010

#### INTRODUCTION

Esters are emitted into the atmosphere from natural (e.g., biomass burning and vegetation) and anthropogenic (e.g., from use as industrial solvents and in perfume and flavoring manufacturing) sources and are

also formed in situ from the oxidation of ethers [e.g., 1-25, and references therein]. Thus, the atmospheric oxidation of these species has the potential to contribute to air quality on regional and global scales. Although the esters are reasonably unreactive (lifetimes against reaction with OH range from a few days to a couple of months for C<sub>3</sub>–C<sub>5</sub> formates and acetates [e.g., 2-4,8,10,19,26,27]) and are not likely major sources of ozone in urban regions [28], their main oxidation products are often soluble organic acids and acid anhydrides [5–15,25,29], which may contribute to

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the atmospheric buildup of condensed-phase organic mass.

As with most volatile organic compounds, atmospheric oxidation is initiated mainly by reaction with OH and leads to the production of a peroxy radical, and subsequently an alkoxy radical, as shown in the following equations for a generic ester,  $RC(O)OCH_2R'$  [30]:

$$OH + RC(=O)OCH_2R'(+O_2)$$
  

$$\rightarrow RC(=O)OCH(OO^{\bullet})R' + H_2O$$
  

$$RC(=O)OCH(OO^{\bullet})R' + NO$$
  

$$\rightarrow RC(=O)OCH(O^{\bullet})R' + NO_2$$

A key step in the oxidation of the esters, and the major source of the organic acids, is the so-called  $\alpha$ -ester rearrangement [5] of the alkoxy radical, which can occur in competition with the reaction of the alkoxy species with O<sub>2</sub>, for example:

$$RC(=O)OCH(O^{\bullet})R' \rightarrow RC(=O)OH + R'C^{\bullet}O$$
$$RC(=O)OCH(O^{\bullet})R' + O_{2}$$
$$\rightarrow RC(=O)OC(=O)R' + HO_{2}$$

The  $\alpha$ -ester rearrangement process was first discovered by Tuazon et al. [5] in their study of the atmospheric oxidation of ethyl, isopropyl, and *t*-butyl acetate, and its occurrence has subsequently been confirmed in theoretical [13,14] and experimental [7–12,15,25] studies of these and other esters, including methyl and ethyl formate, methyl acetate, methyl propionate, methyl pivalate, *n*-propyl acetate and isobutyl acetate. Although it is now apparent that the  $\alpha$ -ester rearrangement occurs more rapidly for larger and more highly substituted alkoxy radicals, there is still limited information available regarding the energetics and dynamics of this process for the suite of atmospherically relevant esters.

In this paper, we describe an environmental chamber study of the oxidation of ethyl formate and ethyl acetate, the major products of the atmospheric oxidation of diethyl ether [16,18,20,31]. These studies were carried out over a range of temperatures (249– 325 K) and O<sub>2</sub> partial pressures (50–700 Torr) to examine competition, under conditions relevant to the lower atmosphere, between the  $\alpha$ -ester rearrangement and the reaction with O<sub>2</sub> for HC(O)OCH(O<sup>•</sup>)CH<sub>3</sub> and CH<sub>3</sub>C(O)OCH(O<sup>•</sup>)CH<sub>3</sub> derived from ethyl formate and ethyl acetate. The data allow activation barriers to the  $\alpha$ -ester rearrangement to be determined, and these values are compared with previous estimates [13–15] for related species.

#### **EXPERIMENTAL**

Experiments were carried out using a 2-m-long, 47-L stainless steel environmental chamber system that has been described previously [15,31,32]. The chamber temperature was controlled using either chilled ethanol (T < 298 K) or heated water (T > 298 K) that was allowed to flow through a jacket surrounding the cell from temperature-regulated circulating baths. Analysis of the gas mixtures in the chamber was conducted using Fourier transform infrared spectroscopy. Multipass optics (modified Hanst-type) housed within the chamber provided an infrared (IR) observational path of 32 m. Infrared spectra were recorded over the range 800-3900 cm<sup>-1</sup> and were obtained at a resolution of 1 cm<sup>-1</sup> from the co-addition of 200 scans (acquisition time 3–4 min).

Experiments involved the irradiation of mixtures of  $Cl_2$  [(14–51) × 10<sup>15</sup> molecule cm<sup>-3</sup>] and the parent ester  $[(0.9-2.5) \times 10^{14} \text{ molecule cm}^{-3}]$  in O<sub>2</sub> (50– 700 Torr)/N<sub>2</sub> (balance) buffer gas at total pressures of 720-770 Torr and at temperatures ranging from 249 to 325 K. Minor components of the gas mixtures were flushed into the chamber from smaller calibrated volumes, using a flow of N<sub>2</sub>, while the O<sub>2</sub> was added directly to the chamber. A xenon-arc lamp, filtered to provide radiation in the 240- to 400-nm range, was used to photolyze Cl<sub>2</sub> and thus initiate the chemistry. Typically, mixtures were photolyzed for four to six periods, each of duration 15-200 s, and an IR spectrum was recorded after each photolysis period. In limited cases, to minimize heterogeneous loss of reaction products, gas mixtures were photolyzed continuously and IR spectra were recorded sequentially throughout the photolysis period.

Quantification of the parent esters (ethyl formate or ethyl acetate) and most major products [formic acid (FA), CO, CO<sub>2</sub>, acetic acid (AA), and acetic acid anhydride (AAn)] was carried out using standard spectra recorded on our system at the temperature at which the experiments were conducted. Quantification of formic acid anhydride (FAn) and acetic formic anhydride (AFAn), both products of ethyl formate oxidation, was via integrated band intensities obtained from room temperature reference spectrum provided by Tim Wallington, Ford Motor Company. Some minor products (e.g., CH<sub>3</sub>OH, CH<sub>2</sub>O, peracetic acid, and AA) were quantified via comparison with reference spectra obtained at 298 K.

A series of control experiments revealed that the two esters under investigation were not subject to significant heterogeneous loss in the chamber and were not photolyzed over the time period of experiments conducted herein. While heterogeneous losses of most major products were minor, it was observed that FA, a major product of ethyl formate oxidation, was prone to significant heterogeneous loss. To minimize this loss, many experiments were conducted using the "continuous photolysis" method. In most cases, corrections (usually <10%) were made to account for this loss. However, results from some early experiments, in which no corrections were made, were indistinguishable from later experiments and were used in the analysis. Quantitative analyses to be presented in this paper are based primarily on yields of FA and AFAn (from ethyl formate) or AA and AAn (from ethyl acetate). These product species are known (or estimated) to react approximately 100 times slower with Cl-atoms than do the parent esters [7,22-24,29,33-36]; hence, no correction for secondary loss of these product species was required.

Chemicals used in this study were from the following sources: Cl<sub>2</sub> (ultrahigh pure; Matheson, Basking Ridge, NJ, USA); ethyl formate (97%), ethyl acetate (99.5+%), AA (99.8%), FA (95%), and AAn (98%+), all from Sigma-Aldrich, Milwaukee, WI, USA; O<sub>2</sub> (U.S. Welding, Denver, CO, USA); N<sub>2</sub> (boil-off from liquid N<sub>2</sub>; U.S. Welding). Gases (Cl<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>) were used as received, and liquids (ethyl formate, ethyl acetate, AA, FA, and AAn) were subjected to several freeze–pump–thaw cycles before use.

### **RESULTS AND DISCUSSION**

#### Ethyl Formate at 298 K

Products identified in the Cl-atom-initiated oxidation of ethyl formate at 298 K included CO<sub>2</sub>, CO, FA, AFAn, peracetic acid, FAn, and, in some cases, trace amounts of formaldehyde and possibly of AA and methanol. On average, these products accounted for about  $86 \pm 15\%$  of the reacted ethyl formate on a carbon basis. Results from typical experiments carried out in air at 1 atm and 298 K, plotted as observed product concentrations versus ethyl formate consumption (appearance profiles), are displayed in Fig. 1. The appearance profiles for CO<sub>2</sub>, CO, FA, AFAn, and peracetic acid are linear within experimental uncertainty, indicating that these may be primary products. However, consideration of the chemistry involved shows that some of the CO and CO<sub>2</sub> result from rapid consumption of reactive first-generation products, such as formaldehyde and acetaldehyde. After removal of spectral features that result from known products, residual absorption features remained in the product spectra at 1115, 1166, 1345, 1455, and 1773  $cm^{-1}$ . Likely contributors to the unidentified absorption features (and to the missing carbon) include hydroperoxides, carbonyls, and alcohols that can be obtained from molecular channels of



Figure 1 Observed (uncorrected) product concentrations versus consumption of ethyl formate following the photolysis of mixtures of  $Cl_2$  and ethyl formate in synthetic air at 720 Torr and 298 K. Symbols represent measured product concentrations, whereas lines represent results from a box-model simulation; see text for details.

		298 K					273 K			255 K	
$P(O_2)$	CO <sub>2</sub>	СО	FA	AFAn	FAn	FA	AFAn	FAn	FA	AFAn	
30									$38 \pm 4$	$27 \pm 3$	
50	$97\pm7$	$46 \pm 5$	$39 \pm 4$	$16 \pm 3$	$4\pm 2$	$29 \pm 4$	$18 \pm 3$	$5\pm 2$	31	30	
150	90	42	39	19	7	24	26	6	21	39	
300	84	35	38	22	7	23	33	6	16	51	
500	78	38	31	26	7	19	37	6	11	50	
700	72	34	28	29	7	14	37	6			

**Table I**Observed (Uncorrected) Product Yields (% of Ethyl Formate Consumed on a Per Mole Basis) as a Function of $O_2$  Partial Pressure from the Cl-Atom-Initiated Oxidation of Ethyl Formate at a Total Pressure of 730  $\pm$  30 Torr

Results shown are from the average of multiple experiments at each  $O_2$  partial pressure. Uncertainties shown at the top of each column apply to all data in that column.

Abbreviations: AFAn, acetic formic anhydride; FA, formic acid; FAn, formic anhydride.

peroxy radical reactions, as discussed in more detail in the following text.

Yields of most products were found to be dependent on  $O_2$  partial pressure (see Table I). Yields of FA,  $CO_2$ , and CO decreased with increasing  $O_2$  pressure, while those of AFAn and FAn increased. As is quantitatively discussed in the following text, the majority of these effects stem from the HC(O)OCH(O•)CH<sub>3</sub> species, whose chemistry involves competition between  $O_2$  reaction to form AFAn and  $\alpha$ -ester rearrangement to, in essence, form FA, CO, and CO<sub>2</sub>.

To quantitatively determine the origin of the identified products, and to examine the origin of the  $O_2$ dependence of their yields, the branching ratios to the three possible sites of Cl-atom attack on ethyl formate must first be determined:

$$Cl + HC(O)OCH_2CH_3 \rightarrow {}^{\bullet}C(O)OCH_2CH_3 + HCl$$
(1a)

$$Cl + HC(O)OCH_2CH_3 \rightarrow HC(O)OCH^{\bullet}CH_3 + HCl$$

(1b)

$$Cl + HC(O)OCH_2CH_3 \rightarrow HC(O)OCH_2CH_2^{\bullet} + HCl$$

(1c)

To determine the branching ratio to reaction at the formate group, reaction (1a), experiments were conducted with NO<sub>2</sub> [(3.5–7) × 10<sup>14</sup> molecule cm<sup>-3</sup>], added to standard Cl<sub>2</sub>/ethyl formate/air mixtures. Under these conditions, the radical product of reaction (1a) is converted quantitatively to a stable PAN-type compound [9,25], designated here as ethoxyPAN or EoPAN:

$$Cl + HC(O)OCH_2CH_3 \rightarrow {}^{\bullet}C(O)OCH_2CH_3 + HCl$$
(1a)

$$^{\bullet}C(O)OCH_{2}CH_{3} + O_{2} \rightarrow ^{\bullet}O_{2}C(O)OCH_{2}CH_{3}$$
(2a)

•
$$O_2C(O)OCH_2CH_3 + NO_2$$
  
→  $O_2NO_2C(O)OCH_2CH_3(EoPAN)$  (3a)

The formation of EoPAN is accompanied by the production of less thermally stable alkyl peroxynitrates, as shown for channel (1b):

$$Cl + HC(O)OCH_2CH_3 \rightarrow HC(O)OCH^{\bullet}CH_3 + HCl$$
(1b)

$$HC(O)OCH^{\bullet}CH_{3} + O_{2} \rightarrow HC(O)OCH(OO^{\bullet})CH_{3}$$

$$HC(O)OCH(OO^{\bullet})CH_{3} + NO_{2}$$
  

$$\leftrightarrow HC(O)OCH(OONO_{2})CH_{3}$$
(3b)

To allow separation of the spectral contributions of EoPAN and the alkyl peroxynitrates, excess NO [(7–55)  $\times 10^{14}$  molecule cm<sup>-3</sup>)] was added to the photolyzed mixtures to remove the alkylperoxynitrate species, for example,

$$HC(O)OCH(OONO_2)CH_3 \rightarrow HC(O)OCH(OO^{\bullet})CH_3 + NO_2 \quad (-3b) HC(O)OCH(OO^{\bullet})CH_3 + NO \rightarrow HC(O)OCH(O^{\bullet})CH_3 + NO_2 \quad (4b) HC(O)OCH(O^{\bullet})CH_3 \rightarrow Products$$

After proper accounting for products generated following NO addition (FA, AFAn, and PAN, see the following text), as well as inorganic species such as CINO<sub>2</sub> and CINO, spectral features centered at 1166,

•

1224, 1300, 1745, and 1835  $cm^{-1}$  could be assigned to EoPAN, whereas major alkyl peroxynitrate features were found at 1100, 1160, 1300, 1727, and 1762 cm<sup>-1</sup>. These features correspond very closely to those attributed [9,37] to the analogous species generated from methyl formate oxidation in the presence of NO<sub>2</sub>, O<sub>2</sub>NO<sub>2</sub>C(O)OCH<sub>3</sub>, and HC(O)OCH<sub>2</sub>OONO<sub>2</sub>. The EoPAN band positions and relative intensities also agree quite well with those reported by Malanca et al. [25] in a recent study of ethyl formate oxidation, the one exception being the 1166 cm<sup>-1</sup> band, which is absent in the spectrum of Malanca et al. [25]. Given this fact, it is likely that the  $1166 \text{ cm}^{-1}$  band is then due not to EoPAN but to the presence in our spectra of other multifunctional nitrates or nitrites derived from oxidation of the ethyl group. Note also that, as shown in the following text, most of the Cl-atom reaction occurs at the -CH<sub>2</sub>- group in ethyl formate and thus the major contributor to the alkylperoxynitrate absorption spectrum is expected to be the  $HC(O)OCH(OONO_2)CH_3$ species.

Determination of the branching ratio to pathway (1a) then requires quantification of the EoPAN formed versus loss of the parent ethyl formate. Spectra of the PAN species formed from methyl, isopropyl, and tbutyl formate oxidation in the presence of NO<sub>2</sub> are available from work in our laboratory [9,38], and all show integrated band strengths (for the band centered near 1830 cm<sup>-1</sup>) of  $(3.9 \pm 0.8) \times 10^{-17}$  cm molecule<sup>-1</sup> and peak cross sections for this band of  $(1.9 \pm 0.4) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ . Use of these values for EoPAN quantification allows us to conclude that  $18 \pm 5\%$  of the reaction of Cl-atoms with ethyl formate occurs via pathway (1a). Equivalently, given  $k_1 \approx 1.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} [22-24,29,33],$ then  $k_{1a} = (1.8 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This result, however, appears to disagree with the yield of EoPAN (and hence the branching to abstraction of the formyl H-atom) reported by Malanca et al. [25],  $44 \pm 5\%$  branching ratio reported in their study compared with our  $(18 \pm 5\%)$  value. However, comparisons of the cross sections used in our work with those of Malanca et al. (provided by the authors of that study via private communication) reveal that their values are roughly a factor of four lower than our estimates. While determination of the exact branching to pathway (1a) awaits clarification of this cross-section issue, we do note that the use of cross sections reported in the study of Malanca et al. [25] for the analysis of our data would lead to a sum of the abstraction pathways well in excess of unity.

To conclude our discussion of pathway (1a), it remains to consider the end products of this pathway in the absence of  $NO_x$ . By analogy to the case of methyl formate, addition of  $O_2$  should be the sole fate of  $^{\circ}C(O)OCH_2CH_3$ . Subsequent reaction of the resultant acylperoxy radical with other peroxy radicals present in the system is expected to generate  $CO_2$  and  $CH_3CHO$  as first-generation end products:

$$C(O)OCH_2CH_3 + O_2 \rightarrow {}^{\bullet}O_2C(O)OCH_2CH_3 \quad (2a)$$
  
$${}^{\bullet}O_2C(O)OCH_2CH_3 + RO_2$$
  
$$\rightarrow {}^{\bullet}OC(O)OCH_2CH_3 + RO^{\bullet} + O_2 \quad (5a)$$
  
$${}^{\bullet}OC(O)OCH_2CH_3 \rightarrow CO_2 + {}^{\bullet}OCH_2CH_3 \quad (6)$$

$$^{\bullet}\text{OCH}_2\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 \qquad (7)$$

Acetaldehyde was not observed in any of the experiments conducted in the absence of  $NO_x$ . However, as acetaldehyde is about eight times more reactive with Cl than ethyl formate [22–24,29,33,34], rapid conversion of this species mainly to CO<sub>2</sub> and CO (via CH<sub>2</sub>O), but also to peracetic acid and AA, would be expected. Thus, to first approximation, in the standard  $NO_x$ -free experiments conducted here, and using our branching ratio value, reaction (1a) will result in the formation of CO<sub>2</sub> and CO with molar yields of  $36 \pm 10\%$  and  $18 \pm 5\%$ , respectively, independent of O<sub>2</sub> partial pressure.

The major focus of this work is related to the products formed from the main site of attack (i.e., at the  $-CH_2$ - group), leading to the formation of  $HC(O)OCH(O_2^{\bullet})CH_3$ .

$$Cl + HC(O)OCH_2CH_3(+O_2)$$
  

$$\rightarrow HC(O)OCH(O_2^{\bullet})CH_3 + HCl \quad (1b,2b)$$

In the absence of  $NO_x$ , this peroxy radical is subsequently converted via reaction with peroxy species to molecular and radical products:

$$HC(O)OCH(O_{2}^{\bullet})CH_{3} + HO_{2}$$

$$\rightarrow HC(O)OCH(OOH)CH_{3} + O_{2} \qquad (8b)$$

$$HC(O)OCH(O_{2}^{\bullet})CH_{3} + RO_{2}$$

$$\rightarrow HC(O)OCH(OH)CH_{3} + R'CHO + O_{2} \qquad (5bi)$$

 $\rightarrow$  HC(O)OC(= O)CH<sub>3</sub> (AFAn) + ROH + O<sub>2</sub> (5bii)

$$\rightarrow$$
 HC(O)OCH(O<sup>•</sup>)CH<sub>3</sub> + RO<sup>•</sup> + O<sub>2</sub> (5biii)

The alkoxy radical product of reaction (5biii),  $HC(O)OCH(O^{\bullet})CH_3$ , may then undergo any of three

possible competing reaction pathways, the  $\alpha$ -ester rearrangement (9), reaction with O<sub>2</sub> (10), or decomposition via C-C bond scission (11):

Note that all three stable products, FA, AFAn, and FAn, were observed in every experiment conducted and thus it is at least possible that all three competing  $HC(O)OCH(O^{\bullet})CH_3$  reaction pathways are operative. However, there is evidence to suggest that the observed FAn is not obtained from reaction (11). First, the appearance profile (Fig. 1) is curved upward, in contrast with the linear appearance profiles observed for AFAn and FA. This suggests that a significant fraction of the observed FAn product is not primary, but instead derives from the oxidation of a primary product. Second, if the majority of the FAn was obtained from reaction (11), its yield would be expected to decrease with

increasing  $O_2$  partial pressure. This is contrary to what is observed—the FAn yield is lowest at low  $O_2$  partial pressure (50 Torr), increases at intermediate  $O_2$  partial pressures, and is essentially independent of  $O_2$  at higher  $O_2$  partial pressures. As discussed further in the following text, it is likely that FAn production results from pathway (1c) rather than (1b). In any event, because the FAn yield is small (<10%), its origin has little effect on the discussion that follows regarding the competition between reactions (9) and (10).

It is clear from Fig. 1 and Table I that in the absence of NO<sub>x</sub> at 298 K, FA and AFAn are the two major organic products obtained from the Cl-atominitiated oxidation of ethyl formate. On average, these two products accounted on a molar basis for  $58 \pm 4\%$ of the oxidized ethyl formate, independent of the O<sub>2</sub> partial pressure (50–700 Torr). Because reactions (9) and (10) represent the dominant pathways for the formation of FA and AFAn (see further discussion in the following text), it follows that the branching ratio to reaction (1b) is at least 54%. Note that the co-product of FA, CH<sub>3</sub>C(O), would be expected [34,39,40] to lead to the production of CO<sub>2</sub>, CO, CH<sub>2</sub>O, peracetic acid, CH<sub>3</sub>OH, and AA, most or all of which are observed.

The competition between reactions (9) and (10) is displayed quantitatively in Fig. 2; as expected, the yield



**Figure 2** Fractional molar yields of formic acid (triangles) and acetic formic anhydride (circles) as a function of O<sub>2</sub> partial pressure at 298 K, obtained from the photolysis of Cl<sub>2</sub>/ethyl formate/O<sub>2</sub>/N<sub>2</sub> mixtures. Solid lines represent fits of the data to Eq. (A), which yielded  $k_9/k_{10} = 4.6 \times 10^{19}$  molecule cm<sup>-3</sup>, C = 0.73; see text for details.

of AFAn increases with increasing O2 partial pressure at the expense of FA. In addition, it is clear that there is a non-zero yield of AFAn at low (zero) O<sub>2</sub> partial pressure. This O<sub>2</sub>-independent component of the AFAn production likely originates from the reaction of the peroxy radical  $HC(O)OCH(O_2^{\bullet})CH_3$  with itself and other peroxy species, reaction (5b), as discussed earlier. Also, competition between reactions (9) and (10) is expected to lead not only to a decrease in the FA yield with increasing O<sub>2</sub> partial pressure but also to a concomitant decrease in the yields of CO and CO<sub>2</sub>. It was observed that the change in the CO yield (from 46 to 34% between 50 and 700 Torr O<sub>2</sub>) was roughly equal to the observed change in the FA (39–28%) and AFAn (16–29%) yields. The observed change in CO<sub>2</sub> yields was measurably higher (96-72%), however, for reasons that are not understood at present.

The yield data for FA and AFAn can be used to obtain the rate coefficient ratio  $k_9/k_{10}$ . From a consideration of the chemistry, the following relation holds:

$$\frac{Y(FA)}{[Y(FA) + Y(AFAn)]} = \frac{C \times k_9}{k_9 + k_{10}[O_2]}$$
(A)

where Y(FA) and Y(AFAn) are the fractional molar yields of FA and AFAn, respectively; C is a scaling term that accounts for sources of AFAn other than from reaction (10);  $k_9$  is the first-order rate coefficient for reaction (9); and  $k_{10}$  is the second-order rate coefficient for reaction (10). Before fitting the data, other sources and losses for FA and AFAn must be considered. As discussed in more detail in the following text, FA production is likely to occur as the result of reaction (1c) and subsequent chemistry, particularly at low O<sub>2</sub> partial pressure. Box-model simulations of the chemistry, using the Acuchem software package [41], show that this source is small-about 4 and 1% of the FA likely originates from (1c) at 50 and 700 Torr O2, respectively. An additional mechanism for FA production is via the reaction of HO<sub>2</sub> with CH<sub>2</sub>O [42] and subsequent chemistry of the resultant complex. Again, simulations indicate that this source is minor, contributing less than 2% of the observed FA at 298 K. To account for these production mechanisms, minor corrections were made to the measured FA yields. As alluded to in the experimental section, losses of FA and AFAn via reaction with Cl-atoms are negligible because these species are approximately 50 and 100 times less reactive with Clatoms than is ethyl formate [7,22–24,29,33,34].

A least-squares fit of the corrected product yield data to Eq. (A), shown in Fig. 3, leads to a 298 K

rate coefficient ratio  $k_9/k_{10} = (4.6 \pm 1.0) \times 10^{19}$ molecule cm<sup>-3</sup>, with  $C = 0.73 \pm 0.05$ . The reported uncertainty in the rate coefficient ratio is an estimate and is dominated by possible systematic errors in our understanding of the chemistry rather than by precision errors in spectral analysis. The results indicate that the  $\alpha$ -ester rearrangement, reaction (9), is about nine times more rapid than reaction (10) with O<sub>2</sub> in air at 1 atm and 298 K and will thus dominate the chemistry of  $HC(O)OCH(O^{\bullet})CH_3$  under these conditions. The rate coefficient ratio is in line with expectations—the rate of the  $\alpha$ -ester rearrangement process for  $HC(O)OCH(O^{\bullet})CH_3$  is intermediate between the rates for the slower methyl formate and methyl acetate cases and that of the more rapid ethyl acetate case [5,7,9,11,13-15].

The data are also broadly consistent with those recently reported by Malanca et al. [25]. The majority of their experiments were conducted in the presence of NO<sub>2</sub> (which opens up different alkoxy radical reaction channels), but the results appear to be in semiquantitative agreement with what is reported here. Malanca et al. [25] report that  $62 \pm 8\%$  of the reaction occurs at the CH<sub>2</sub> group, in agreement with our findings. In their system,  $HC(O)OCH(O^{\bullet})CH_3$  not only can undergo reactions (9) and (10) but can also react with NO2 to produce the nitrate species, HC(O)OCH(ONO<sub>2</sub>)CH<sub>3</sub>. Their results show roughly equal (combined) occurrence of the two bimolecular reaction pathways and the  $\alpha$ -ester rearrangement in O<sub>2</sub> at 1 atm, broadly consistent with our findings. (Note that exact comparisons between our data and those of Malanca et al. are not possible because, first, the [NO<sub>2</sub>] used in the study of Malanca et al. changed over the course of an experiment because of its photolysis and, second, the conversion of HC(O)OCH(OO•)CH<sub>3</sub> to HC(O)OCH(O•)CH<sub>3</sub> occurred via its reaction with NO in their work, which opened up the possibility of an influence of chemical activation on the chemistry of the nascent, internally excited HC(O)OCH(O $^{\bullet}$ )CH<sub>3</sub> [e.g., 7,9,15].) In the absence of NO<sub>2</sub> (i.e., under conditions similar to our work), Malanca et al. [25] reported the formation of FA and AFAn in a 2:1 ratio in O<sub>2</sub> at 1 atm. This ratio is higher than the roughly 1:1 ratio reported in our study, which may be a consequence of different radical densities in the two studies, and hence the different relative occurrences of various RO<sub>2</sub>-RO<sub>2</sub> reactions, which could impact the overall AFAn yield. A more complete summary of rates and barriers for  $\alpha$ -ester rearrangement reactions, and the dependencies of these parameters on radical structure, will be presented in a later section.

It remains to consider the reaction of Cl-atoms at the CH<sub>3</sub>-group in ethyl formate, which will generate



**Figure 3** Product yield data  $\{Y(FA)/[Y(FA) + Y(AFAn)]\}$  obtained from Cl-atom-initiated oxidation of ethyl formate as a function of O<sub>2</sub> partial pressure. Symbols represent measured data: solid circles, 325 K; open triangles, 298 K; solid squares, 273 K; and open triangles, 255 K. Solid lines are fits to the data at each individual temperature, whereas dashed lines are results of a fit to the entire data set; see text for details.

HC(O)OCH<sub>2</sub>CH<sub>2</sub>O<sub>2</sub><sup>•</sup>:

$$Cl + HC(O)OCH_2CH_3(+O_2) \rightarrow HC(O)OCH_2CH_2O_2^{\bullet}$$
(1c)

Note that, given the discussion just presented, the branching to channel (1c) cannot exceed approximately 25%. Chemistry associated with this peroxy species includes the following:

$$HC(O)OCH_2CH_2O_2^{\bullet} + RO_2$$

$$\rightarrow \text{HC}(\text{O})\text{OCH}_2\text{CH}_2\text{O}^{\bullet} + \text{RO} + \text{O}_2 \tag{5c1}$$

$$\rightarrow$$
 HC(O)OCH<sub>2</sub>CH<sub>2</sub>OH + R'CHO + O<sub>2</sub> (5cii)

$$\rightarrow$$
 HC(O)OCH<sub>2</sub>CHO + ROH + O<sub>2</sub> (5ciii)

 $HC(O)OCH_2CH_2O_2^{\bullet} + HO_2$ 

$$\rightarrow$$
 HC(O)OCH<sub>2</sub>CH<sub>2</sub>OOH + O<sub>2</sub> (8c)

Subsequent reactions of the resulting alkoxy species,  $HC(O)OCH_2CH_2O^{\bullet}$ , may then include decomposition, isomerization via a 1,5-H atom shift, and/or  $O_2$ 

reaction:

(13)

$$HC(O)OCH_2CH_2O^{\bullet} + O_2$$
  

$$\rightarrow HC(O)OCH_2CHO + HO_2$$
(14)

From previous studies of methyl formate oxidation [9,15], the HC(O)OCH<sub>2</sub> product of reaction (12) will, via the HC(O)OCH<sub>2</sub>O<sup>•</sup> species, in part produce FAn and FA:

$$HC(O)OCH_2O^{\bullet} + O_2 \rightarrow HC(O)OCHO(FAn) + HO_2$$
(15)

$$HC(O)OCH_2O^{\bullet} \rightarrow HC(O)OH(FA) + HCO$$

(16)

Given the small branching fraction to pathway (1c), our inability to identify species such as HC(O)OCH<sub>2</sub>CHO

in the IR spectra, and the multiple possible sources of species such as CO, CH<sub>2</sub>O, and CO<sub>2</sub>, it is not possible to draw quantitative conclusions regarding the entire end product distribution resulting from pathway (1c). Nonetheless, this channel likely represents the source of FAn in our experiments, as well as a minor source of FA as discussed previously with regard to the determination of the rate coefficient ratio  $k_9/k_{10}$ . The appearance profile for FAn is curved upward, suggesting that it is at least, in part, a secondary product. This behavior may be due to the intermediacy of species such as HC(O)OCH<sub>2</sub>CH<sub>2</sub>OH, HC(O)OCH<sub>2</sub>CHO, and HC(O)OCH<sub>2</sub>CH<sub>2</sub>OOH, formed from reactions (5c) or (8c) or analogous products formed from the  $HC(O)OCH_2O_2$  chemistry. Also, we note that the FAn yield is lowest at low O<sub>2</sub> partial pressure (50 Torr) and essentially independent of O<sub>2</sub> at higher O<sub>2</sub> partial pressures as would be expected from competition involving reactions (15) and (16) [9,15].

As a consistency check, a comparison between measured data and a box-model simulation of the chemistry for experiments conducted at 298 K in the presence of 150 Torr O<sub>2</sub> is presented (see Fig. 1). Problems in accurately representing the chemistry in the model originate from a lack of quantitative knowledge of the relevant peroxy radical chemistry (e.g., rates and branching in the selfreaction of  $HC(O)OCH(OO^{\bullet})CH_3$  and the subsequent fate of molecular products of this chemistry (e.g., HC(O)OCH(OOH)CH<sub>3</sub>). In general, measurementmodel agreement was best when molecular channels of RO<sub>2</sub>-RO<sub>2</sub> reactions were kept low. In the comparison shown, branching ratios of 10% to molecular channels were assumed. For reactions involving either HO<sub>2</sub> or acyl peroxy radicals, total rate coefficients of 10<sup>-11</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> were used, whereas for all other RO2-RO2 reactions, total rate coefficients of 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> were assumed. Despite the obvious limitations, there is generally good agreement between the measured and modeled concentrations of the major products. The most obvious model-measurement disagreements involve CO<sub>2</sub>, for which the measurements are higher than the model, and AFAn, for which the reverse is true. Spurious production of CO<sub>2</sub> is often observed upon irradiation of the chamber and may contribute to the observed disagreement. In the case of AFAn, a major source of this species in the model is from the formation and subsequent destruction of HC(O)OCH(OOH)CH<sub>3</sub>.

 $HC(O)OCH(OO^{\bullet})CH_3 + HO_2$ 

 $\rightarrow \text{HC(O)OCH(OOH)CH}_3 + O_2$  (8b)  $\text{Cl} + \text{HC(O)OCH(OOH)CH}_3 \rightarrow \rightarrow \text{HC(O)OC(O)CH}_3$ 

Loss of this species via other routes (possibly heterogeneous) in the chamber could contribute to the modelmeasurement discrepancy.

As a possible solution to some of these measurement-model discrepancies, an anonymous reviewer pointed out the possibility of an additional channel in the chemistry of HC(O)OCH(O $\bullet$ )CH<sub>3</sub>, a unimolecular 1,4-H shift as shown in the following equation:

$$HC(O)OCH(O^{\bullet})CH_3 \rightarrow {}^{\bullet}C(O)OCH(OH)CH_3$$

which would lead to CO<sub>2</sub> and CH<sub>3</sub>CHO as likely end products. While we cannot rule out the occurrence of this channel altogether, a reexamination of our yield data (in particular, the FA data and their dependence on O<sub>2</sub> partial pressure) indicates that this can at most be a minor channel—we estimate a maximum occurrence of 25% relative to the  $\alpha$ -ester reaction, which would lead to a concomitant 25% increase in our reported  $k_9/k_{10}$  ratios.

To conclude this section, we note that Sellevåg and Nielsen [29] also reported on a brief study of the Clinitiated oxidation of ethyl formate in air. Major products observed were FA, CO, and CO<sub>2</sub>, consistent with our findings. However, these authors postulated that these species are formed following Cl-atom attack at the methyl group, inconsistent with the interpretation presented here and in [25] and with the now wellestablished occurrence of the  $\alpha$ -ester rearrangement.

#### Ethyl Formate versus Temperature: Chemistry of HC(O)OCH(O<sup>•</sup>)CH<sub>3</sub>

The oxidation of ethyl formate was also studied above (325 K) and below (273 and 255 K) ambient temperature. At 325 K, products observed were FA, AFAn, CO, CO<sub>2</sub>, peracetic acid, FAn, and, possibly, trace amounts of CH<sub>2</sub>O in some cases. In general, yields were similar to those found at 298 K; however, unlike room temperature, yields of most products (e.g., CO,  $44 \pm 4\%$ ; FA,  $45 \pm 3\%$ ; AFAn,  $12 \pm 2\%$ ; and peracetic acid,  $\approx 6\%$ ) were found to be independent of O<sub>2</sub> partial pressure. Yields of CO<sub>2</sub> were in the range 80–100%, with a possible (weak) inverse correlation with O<sub>2</sub> partial pressure. The only species showing a distinct dependence on O<sub>2</sub> partial pressure was FAn, whose yield increased from about 1.5–2% in the presence of 50 Torr O<sub>2</sub> to about 5% in 700 Torr O<sub>2</sub>.

This independence of the yields of the main products on  $O_2$  partial pressure is attributed to the rapidity of the  $\alpha$ -ester rearrangement at elevated temperature. The only significant source of AFAn under these conditions is from molecular channels of reactions involving HC(O)OCH(O<sub>2</sub>)CH<sub>3</sub> with peroxy species, whereas essentially all HC(O)OCH(O<sup>•</sup>)CH<sub>3</sub> radicals are converted to FA via reaction (9) even at high O<sub>2</sub> partial pressure. As was the case at 298 K, the dependence of the FAn yield on O<sub>2</sub> partial pressure is consistent with competition between reactions (15) and (16),  $k_{16}/k_{15} = (4.8 \pm 0.7) \times 10^{18}$  molecule cm<sup>-3</sup> at 324 K [15]. Simulations indicated that the formation of FA via the reaction of HO<sub>2</sub> with CH<sub>2</sub>O was not significant at this temperature because of rapid decomposition of the HO<sub>2</sub>-CH<sub>2</sub>O adduct [42].

While the negligible variation in the FA/AFAn ratio on O<sub>2</sub> partial pressure does not allow for an accurate, independent determination of  $k_9/k_{10}$  at 325 K, examination of the observed product ratio versus O<sub>2</sub> partial pressure data allows us to conclude that  $k_9/k_{10} > 1.4 \times 10^{20}$  molecule cm<sup>-3</sup>. A global fit to the entire data set, presented in detail in the following text, gives  $k_9/k_{10} = 2.0 \times 10^{20}$  molecule cm<sup>-3</sup>, consistent with this lower limit.

Products observed at low temperature (273 and 255 K) were FA, AFAn, CO, and CO<sub>2</sub>, whereas FAn and trace amounts of CH2O were also observed at 273 K. These products typically accounted for 65-70% of the reacted ethyl formate. As is evident from Table I, yields of most products showed a strong correlation with O<sub>2</sub> partial pressure: AFAn formation was favored at high O<sub>2</sub> pressure at the expense of FA, CO, and CO<sub>2</sub>, consistent with competition between reactions (9) and (10). The FAn yield ( $\approx 6\%$ ), however, was independent of O<sub>2</sub>, consistent with its formation from attack at the CH<sub>3</sub>-group in ethyl formate [e.g., reactions (1c), (5ci), (12), and (15)]. Note that at reduced temperature, reaction (15) is strongly favored over reaction (16) even at 50 Torr O<sub>2</sub> [15]. This observed independence of the FAn yield on O<sub>2</sub> is strong evidence for negligible formation of FA from reaction (16) at reduced temperature.

Before using the O<sub>2</sub> dependence of the FA and AFAn yields to determine  $k_9/k_{10}$  values at reduced temperature, FA formation from HO2-CH2O adduct chemistry was first accounted for. Box-model simulations of the reaction system indicated that approximately 10% ( $\approx$ 25%) of the observed FA was originating from this chemistry at 273 (255) K. After correction, it was found that the sum of the FA and AFAn yields was essentially independent of temperature, an indication that the magnitude of the correction applied is reasonable. Note also that the determination of  $k_9/k_{10}$  ratios is not overly sensitive to this correction, as the FA concentration appears in both the numerator and denominator in Eq. (A) and the applied correction is independent of  $[O_2]$ . The corrected yield data are shown in Fig. 3. Fits to the data (at each temperature,

independently) yielded  $k_9/k_{10} = (1.53 \pm 0.35) \times 10^{19}$ molecule cm<sup>-3</sup> at 273 K and (0.42 ± 0.14) × 10<sup>19</sup> molecule cm<sup>-3</sup> at 255 K.

Finally, a least-squares fit was performed on the entire data set (i.e., the data obtained at all temperatures studied). Here, the rate coefficient ratio  $k_9/k_{10}$  was represented in the fit by two parameters, that is,  $k_9/k_{10} = A \exp(-B/T)$ , whereas the scaling factor *C* was determined independently at each temperature. This global fit yielded  $k_9/k_{10} = 1.8 \times 10^{26} \exp(-4466/T)$  molecule cm<sup>-3</sup>. Rate coefficient ratios obtained from fits to the individual temperatures, as well as those obtained from the global fit, are given in Table II; very good agreement is seen between the two sets of data. Comparisons of these data with rate data on the  $\alpha$ -ester rearrangement in other esters will be made in a later section.

#### Ethyl Acetate at 298 K

Products observed from the Cl-atom-initiated oxidation of ethyl acetate at 298 K were AA, AAn, CO, CO<sub>2</sub>, CH<sub>2</sub>O, and, possibly, traces of peracetic acid and AFAn. The identified products accounted for, on average, 75  $\pm$  15% of the reacted ethyl acetate on a carbon atom basis. Additional absorption features at 940, 1040, 1075, 1122, 1200, 1230, 1255, 1337, 1381, 1444, 1742, and 1790 cm<sup>-1</sup> were also noted and are likely associated with stable end products, such as CH<sub>3</sub>C(O)OCH(OOH)CH<sub>3</sub> or CH<sub>3</sub>C(O)OCH(OH)CH<sub>3</sub>, of RO<sub>2</sub>–RO<sub>2</sub> and RO<sub>2</sub>–HO<sub>2</sub> chemistry.

Results from a typical experiment (conducted in O<sub>2</sub> at 150 Torr, with a total pressure of 750 Torr) are shown in Fig. 4. Appearance profiles of AA, AAn, and CO<sub>2</sub> are linear, indicating the likelihood that these are primary products of the ethyl acetate oxidation. Evidence for the conversion of CH<sub>2</sub>O (appearance profile curved downward) to CO (appearance profile curved upward) is seen in the data, as expected given the high relative reactivity of formaldehyde with Cl-atoms ( $k_{Cl+CH_2O}/k_{Cl+CH_3C(O)OCH_2CH_3} \approx 4$ ) [33–36].

Yields of the product species were found to be noticeably (but weakly) dependent on O<sub>2</sub> partial pressure, see the summary in Table III, with the yield of AAn increasing with increasing O<sub>2</sub> partial pressure at the expense of the other species (AA, CO<sub>2</sub>, and possibly the sum of CO + CH<sub>2</sub>O). Similar to the ethyl formate study, and as presented in quantitative detail in the following text, the source of this O<sub>2</sub> dependence stems from a competition between the  $\alpha$ -ester rearrangement (R20) of CH<sub>3</sub>C(O)OCH(O<sup>•</sup>)CH<sub>3</sub> and its reaction (21)

$k_9/k_{10}$ (molecule cm <sup>-3</sup> ),		
$k_9/k_{10}$ (molecule cm <sup>-3</sup> ), from Global Fit to Entire Data Set		
$(20 \pm 7) \times 10^{19}$		
$(5.5 \pm 1.0) \times 10^{19}$		
$(1.4 \pm 0.4) \times 10^{19}$		
$(0.44 \pm 0.14) \times 10^{19}$		

**Table II** Rate Coefficient Ratios  $k_9/k_{10}$  Obtained from Fits of Formic Acid and Acetic Formic Anhydride Yield Data to Eq. (A)

Ratios shown are from fits to the data from each temperature individually, or from a global fit to the complete data set; see text for details.

**Table III**Observed (Uncorrected) Product Yields (% of Ethyl Acetate Consumed on a Per Mole Basis) as a Function of $O_2$  Partial Pressure from the Cl-atom Initiated Oxidation of Ethyl Acetate at a Total Pressure of 730  $\pm$  30 Torr

$P(O_2)$	325 K		298 K			273 K		249 K	
	AA	AAn	CO <sub>2</sub>	AA	AAn	AA	AAn	AA	AAn
50	$64 \pm 4$	$18 \pm 3$	$65\pm 6$	$55 \pm 4$	$21 \pm 3$	$56 \pm 4$	$29 \pm 3$	$50 \pm 4$	$33 \pm 3$
50								50	35
150	66	20	64	53	26	47	30	42	43
150						48	31	39	44
300	63	19	64	52	26	49	35	32	48
400	61	19						31	54
500	57	18	55	48	30	41	43	25	53
700	60	22	51	52	32	35	40	26	61
700								22	55

Results shown are from the average of multiple experiments at each  $O_2$  partial pressure. Uncertainties shown at the top of each column apply to all data in that column.

Abbreviations: AA, acetic acid; AAn, acetic acid anhydride.



Figure 4 Observed (uncorrected) product concentrations versus consumption of ethyl acetate following the photolysis of mixtures of  $Cl_2$  and ethyl acetate in synthetic air at 750 Torr and 298 K. Open circles,  $CO_2$ ; filled circles, acetic acid; open triangles, CO; filled triangles, acetic formic anhydride (AAn); and squares, formaldehyde. Lines are linear least-squares fits to the  $CO_2$ , acetic acid, and AAn data.

with O<sub>2</sub>:

$$Cl + CH_3C(O)OCH_2CH_3$$
  

$$\rightarrow CH_3C(O)OCH^{\bullet}CH_3 + HCl \qquad (17a)$$

$$CH_3C(O)OCH^{\bullet}CH_3 + O_2$$

$$\rightarrow CH_3C(O)OCH(OO^{\bullet})CH_3$$
(18)

 $CH_3C(O)OCH(OO^{\bullet})CH_3 + RO_2$ 

$$\rightarrow CH_3C(O)OCH(O^{\bullet})CH_3 + RO^{\bullet} + O_2 \qquad (19)$$

$$CH_3C(O)OCH(O^{\bullet})CH_3 \rightarrow CH_3C(O)OH + CH_3C(O)$$

(20)

 $O_2$ 

$$CH_{3}C(O)OCH(O^{\bullet})CH_{3} + O_{2}$$
  

$$\rightarrow CH_{3}C(O)OC(O)CH_{3} (AAn) + HO_{2}$$
(21)

The sum of the AAn and AA yields was 79  $\pm$  5%, independent of O<sub>2</sub> partial pressure, implying that at least 74% of the reaction of Cl-atoms with ethyl acetate proceeds via abstraction from the -CH<sub>2</sub>- group (assuming no other sources of these end products exists, an assumption that is verified in the following text). Given the possibility of the conversion of CH<sub>3</sub>C(O)OCH(OO<sup>•</sup>)CH<sub>3</sub> to other stable products [e.g., CH<sub>3</sub>C(O)OCH(OH)CH<sub>3</sub> and CH<sub>3</sub>C(O)OCH(OOH)CH<sub>3</sub>], it is then possible that the branching ratio to reaction (17a) is considerably greater than 74%.

Before using the AA and AAn product yield data to assess the magnitude of the rate coefficient ratio  $k_{20}/k_{21}$ , it is important to consider other potential sources and sinks for these product species. The reaction of Cl-atoms with AA is about 650 times slower than that for ethyl acetate [33–36]. The reaction of Cl with AAn has not been measured but is anticipated to be similar in magnitude to that for AA. Thus, losses of either product via this route are negligible.

In addition to its formation via reaction (21), AAn may also form via molecular channels of the  $CH_3C(O)OCH(OO^{\bullet})CH_3$  chemistry, for example,

$$2CH_{3}C(O)OCH(OO^{\bullet})CH_{3}$$

$$\rightarrow CH_{3}C(O)OCH(OH)CH_{3} + AAn + CH_{3}C(O)OCH(OO^{\bullet})CH_{3} + HO_{2}$$

$$\rightarrow CH_{3}C(O)OCH(OOH)CH_{3} + O_{2}$$

$$Cl + CH_{3}C(O)OCH(OH)CH_{3}(+O_{2})$$

$$\rightarrow AAn + HO_{2} + HCl$$

$$Cl + CH_{3}C(O)OCH(OOH)CH_{3}$$

$$\rightarrow AAn + OH + HCl$$

These  $O_2$ -independent channels will be accounted for in the analysis in the following text. Additional sources of AA also exist. For example, the coproduct of AA in reaction (20) is CH<sub>3</sub>C(O), itself a possible source of additional AA [34,39,40]:

$$\begin{array}{l} {\rm CH_3C(O)} + {\rm O_2} \to {\rm CH_3C(O)O_2} \\ {\rm CH_3C(O)O_2} + {\rm CH_3C(O)O_2} \to 2({\rm CH_3} + {\rm CO_2}) + {\rm O_2} \\ {\rm CH_3C(O)O_2} + {\rm RO_2} \to {\rm CH_3} + {\rm CO_2} + {\rm O_2} + {\rm RO} \\ {\rm CH_3C(O)O_2} + {\rm HO_2} \\ \to {\rm CH_3} + {\rm CO_2} + {\rm O_2} + {\rm OH} \quad (40\% \ ) \\ \to {\rm CH_3C(O)OH} + {\rm O_3} \quad (15\% \ ) \\ \to {\rm CH_3C(O)OH} + {\rm O_2} \quad (45\% \ ) \end{array}$$

However, no peracetic acid was conclusively detected in any of the 298 K ethyl acetate experiments carried out (yield < 10%) and thus it is unlikely that any significant AA production occurred via this mechanism.

The possible formation of AA from Cl-atom reaction with ethyl acetate at sites other than the CH<sub>2</sub> group must also be considered. On the basis of mechanistic data regarding the reaction of Cl with AA and methyl acetate [7,15,34], reaction at the acetate group probably contributes less than 1% to the overall reaction of Cl-atoms with ethyl acetate. Given the product yields discussed previously, it is then possible that a measurable ( $\leq 25\%$ ) fraction of the reactivity occurs at the CH<sub>3</sub> end of the ethyl fragment:

$$Cl + CH_{3}C(O)OCH_{2}CH_{3}$$

$$\rightarrow CH_{3}C(O)OCH_{2}CH_{2}^{\bullet} + HCl \qquad (17b)$$

$$CH_{3}C(O)OCH_{2}CH_{2}^{\bullet} + O_{2}$$

$$\rightarrow CH_{3}C(O)OCH_{2}CH_{2}OO^{\bullet}$$

$$CH_{3}C(O)OCH_{2}CH_{2}OO^{\bullet} + RO_{2}$$

$$\rightarrow CH_{3}C(O)OCH_{2}CH_{2}O^{\bullet} + RO + O_{2}$$

Likely fates of the resultant alkoxy species,  $CH_3C(O)OCH_2CH_2O^{\bullet}$ , include reaction with O<sub>2</sub>, or decomposition:

$$CH_{3}C(O)OCH_{2}CH_{2}O^{\bullet} + O_{2}$$
  

$$\rightarrow CH_{3}C(O)OCH_{2}CHO + HO_{2}$$
  

$$CH_{3}C(O)OCH_{2}CH_{2}O^{\bullet} \rightarrow CH_{3}C(O)OCH^{\bullet}_{2} + CH_{2}O$$

In either case, the possibility for the formation of  $CH_3C(O)OCH_2O^{\bullet}$ , and hence AA, must be



**Figure 5** Product yield data  $\{Y(AA)/[Y(AA) + Y(AAn)]\}$ , where AA is acetic acid and AAn is acetic formic anhydride, obtained from Cl-atom-initiated oxidation of ethyl acetate as a function of O<sub>2</sub> partial pressure. Symbols represent measured data: solid circles, 325 K; open circles, 298 K; solid triangles, 273 K; and open triangles, 249 K. Solid lines are fits to the data at each individual temperature, whereas dashed lines are results of a fit to the entire data set; see text for details.

considered [7,15]:

$$\begin{array}{ll} CH_{3}C(O)OCH_{2}O^{\bullet}+O_{2}\\ \rightarrow CH_{3}C(O)OC(O)H\,(AFAn)+HO_{2} & (22)\\ CH_{3}C(O)OCH_{2}O^{\bullet}\rightarrow CH_{3}C(O)OH+HCO & (23)\\ HCO+O_{2}\rightarrow HO_{2}+CO \end{array}$$

Previous studies of methyl acetate oxidation [7,15] show that reactions (22) and (23) are competitive at 298 K and occur with essentially equal rates in air at 1 atm. However, given that AFAn could not be conclusively identified in any of the 298 K ethyl acetate experiments conducted (yield < 5%, even at high O<sub>2</sub> partial pressures), it can be concluded that this route provides at most a very minor source of AA.

It is thus apparent that the observed AFAn and AA product yields can be used to determine  $k_{20}/k_{21}$ , as follows:

$$\frac{Y(AA)}{[Y(AA) + Y(AAn)]} = \frac{D \times k_{20}}{(k_{20} + k_{21}[O_2])}$$
(B)

where Y(AA) and Y(AAn) are the fractional molar yields of AA and AAn, respectively; D is a scaling

term that accounts for sources of AAn other than from reaction (21);  $k_{20}$  is the first-order rate coefficient for reaction (20); and  $k_{21}$  is the second-order rate coefficient for reaction (21). Least-squares fitting of the data measured at 298 K to this expression yields  $k_{20}/k_{21} =$  $1.2 \times 10^{20}$  molecule cm<sup>-3</sup>, with D = 0.72 (see Fig. 5). On the basis of test fits conducted with product yields varied over ranges determined by precision and possible systematic errors, the uncertainty on the retrieved rate coefficient ratio is estimated to be  $\pm 50\%$ . The relatively large magnitude of the uncertainty is due largely to the fact that there is only a weak change in the product yields with O<sub>2</sub> partial pressure. Despite the inherent uncertainty in the measured rate coefficient ratio, it is apparent that the  $\alpha$ -ester rearrangement will dominate the chemistry of CH<sub>3</sub>C(O)OCH(O<sup>•</sup>)CH<sub>3</sub> at 298 K, occurring about 24 times more rapidly than its reaction with O<sub>2</sub> in air at 1 atm. This result confirms earlier laboratory and theoretical findings [5,11,13]. Tuazon et al. [5], in their initial discovery of the  $\alpha$ -ester process, found a 96  $\pm$  8% yield of AA and a less than 5% yield of AAn in the OH-initiated oxidation of ethyl acetate in air at 1 atm and 298 K, entirely consistent with the 96%:4% ratio predicted by our rate coefficient ratio. In a similar OH-initiated experiment, Picquet-Varrault

et al. [11] also found a high ratio of AA (75  $\pm$  13%) to AAn (2  $\pm$  1%) but also reported the formation of measurable (15  $\pm$  5% yield) amounts of acetoxyacetaldehyde, CH<sub>3</sub>C(O)OCH<sub>2</sub>CHO. More general conclusions regarding the rate of the  $\alpha$ -ester rearrangement for a range of radicals of the form RC(O)OCH(O<sup>•</sup>)R, including comparisons with theoretical studies [13,14], are made in the following text.

## Ethyl Acetate Oxidation as a Function of Temperature

The oxidation experiments of ethyl acetate were also carried out above (325 K) and below (273 and 249 K) ambient temperature, over a range of  $O_2$  partial pressures (50–700 Torr). At all temperatures studied, observed products (AA, AAn, CO, CO<sub>2</sub>, lesser amounts of CH<sub>2</sub>O, AFAn, and possibly peracetic acid) and mass balances (75–85%) were very similar to those seen at 298 K.

At 325 K, the sum of the yields of AA and AAn was 81  $\pm$  5%, independent of O<sub>2</sub>. The AAn to AA product yield ratio increased very slightly with increasing O<sub>2</sub> partial pressure (see Table III), whereas CO and CO<sub>2</sub> yields showed no discernible O<sub>2</sub> dependence. Fits of the observed AA and AAn yield data to Eq. (B), shown in Fig. 5, yielded  $k_{20}/k_{21} = 3.5 \times 10^{20}$  molecule cm<sup>-3</sup>. Uncertainties on this ratio are quite large, however, because of the weak dependence of the product ratio on O<sub>2</sub> partial pressure over the accessible range, and a more conservative estimate of  $k_{20}/k_{21} > 1.5 \times 10^{20}$  molecule cm<sup>-3</sup> is presented on the basis of the 325 K data alone.

Product yields at reduced temperature (summarized in Table III) showed a more pronounced dependence on O<sub>2</sub> partial pressure (again with AAn increasing with increasing O<sub>2</sub> partial pressure at the expense of AA, CO, and CO<sub>2</sub>) because of the slower rate of occurrence of the  $\alpha$ -ester rearrangement and thus a closer competition between this rearrangement and the O<sub>2</sub> reaction (21). On the basis of low (or undetectable) yields of AFAn and peracetic acid in these low-temperature studies, production of AA either from chemistry of the CH<sub>3</sub>CO<sup>•</sup> product of the  $\alpha$ -ester rearrangement or from chemistry of CH<sub>3</sub>C(O)OCH<sub>2</sub>O<sup>•</sup> is deemed negligible. Fitting of the measured AA and AAn yields at each individual temperature to Eq. (B), as shown in Fig. 5, yielded  $k_{20}/k_{21} = (5.3 \pm 2.0) \times 10^{19}$  molecule cm<sup>-3</sup> at 273 K and  $k_{20}/k_{21} = (2.1 \pm 0.7) \times 10^{19}$  molecule cm<sup>-3</sup> at 249 K.

A fit of the entire ethyl acetate data set (i.e., data obtained at all temperatures) to Eq. (B) was also carried out (see Table IV). Here, the rate coefficient ratio  $k_{20}/k_{21}$  was expressed in the Arrhenius form,  $k_{20}/k_{21} = A \exp(-B/T)$ , with A and B as fit parameters, whereas the scaling factor, D, at each temperature was fitted independently. Best fit, as shown by the dashed curves in Fig. 5, was obtained with  $k_{20}/k_{21} =$  $1.4 \times 10^{24} \exp(-2765/T)$  molecule cm<sup>-3</sup>. However, it was found that very reasonable fits could also be obtained for a fairly wide range of values of A [ $\approx$ (0.4– 10)  $\times$  10<sup>24</sup>] and *B* ( $\approx$ 2400–3300 K), with the two variables strongly correlated. For all reasonable fits, retrieved rate coefficients at reduced temperature remained tightly constrained,  $k_{20}/k_{21} = (1.9-2.2) \times$  $10^{19}$  molecule cm<sup>-3</sup> at 249 K and  $k_{20}/k_{21} = (5.1 - 10^{19})$  $(6.2) \times 10^{19}$  molecule cm<sup>-3</sup> at 273 K. However, more substantial variation was seen in the retrieved rate coefficient ratios at elevated temperatures-in essence, the yield data at 298 K and above do not vary sufficiently with O2 partial pressure to constrain the overall fit.

Including the work presented here, there are now temperature-dependent data [15] for the rate of occurrence of the  $\alpha$ -ester rearrangement (relative to reaction with O<sub>2</sub>) for four radicals, those of formula RC(O)OCHR'O<sup>•</sup>, R and R' = H or CH<sub>3</sub>. The four sets of measurements are summarized in Fig. 6. Generally, an increase in the rate of the  $\alpha$ -ester rearrangement relative to O<sub>2</sub> reaction is seen upon the substitution of CH<sub>3</sub> for H. Near 298 K, the rearrangement occurs three to four times faster for the acetate than for the corresponding formate whereas substitution of an ethyl for a methyl group in the parent ester leads to

**Table IV** Rate Coefficient Ratios  $k_{20}/k_{21}$  Obtained from Fits of AA and AAn Yield Data to Eq. (B)

$k_{20}/k_{21}$ (molecule cm <sup>-3</sup> ), from Separate Fits to Data at Each T	$k_{20}/k_{21}$ (molecule cm <sup>-3</sup> ), from Global Fit to Entire Data Set		
>15 × 10 <sup>19</sup>	$(28 \pm 15) \times 10^{19}$		
$(12 \pm 6) \times 10^{19}$	$(13 \pm 6) \times 10^{19}$		
$(5.3 \pm 2.0) \times 10^{19}$	$(5.4 \pm 2.0) \times 10^{19}$		
$(2.1 \pm 0.7) \times 10^{19}$	$(2.1 \pm 0.7) \times 10^{19}$		
	$\frac{k_{20}/k_{21} \text{ (molecule cm}^{-3}),}{\text{from Separate Fits to Data at Each }T}$ $>15 \times 10^{19}$ $(12 \pm 6) \times 10^{19}$ $(5.3 \pm 2.0) \times 10^{19}$ $(2.1 \pm 0.7) \times 10^{19}$		

Ratios shown are from fits to the data from each temperature individually, or from a global fit to the complete data set; see text for details.



**Figure 6** Rate coefficient data for the  $\alpha$ -ester rearrangement (relative to its reaction with O<sub>2</sub>) for methyl formate (open triangles), methyl acetate (filled triangles), ethyl formate (open circles), and ethyl acetate (filled circles). Solid lines are fits of the simple Arrhenius expression,  $k_{\alpha-\text{ester}}/k_{O_2} = A \exp(-B/T)$ , to the measured data. Dashed lines are obtained by fitting the entire data set simultaneously under the assumption that the A-factor is identical for all four systems; see text for details. Methyl formate and methyl acetate data are those reported in [15].

roughly a factor of 30 increase. Because of uncertainties in the measurements and because the data span a fairly narrow temperature range, however, trends in Afactors and energy barriers with structure are not readily apparent from the data. However, on the basis of other alkoxy radical reactions (e.g., thermal decomposition and isomerization) [43,44], it seems reasonable to assume that A-factors for the set of  $\alpha$ -ester rearrangements are more or less independent of molecular structure and that changes in rate are mostly associated with changes in the activation energy. Thus, a fit of the data for all species was conducted, excluding the 325 K data points from ethyl acetate and ethyl formate (which are too high to be accurately determined), with the A-factor ratio fixed to a constant value for all four reactions and the activation energy for each compound determined as a fit parameter. Best fit, shown in Fig. 6, was obtained for  $A_{\alpha-\text{ester}}/A_{\text{O}_2} = 3.3 \times 10^{25}$ molecule cm<sup>-3</sup> and activation energy differences of about 10.0, 9.2, 8.0, and 7.2 kcal/mole for methyl formate, methyl acetate, ethyl formate, and ethyl acetate, respectively. Given that typical activation energies for the reaction of small alkoxy radicals with O2 fall in the range 0–1 kcal/mole [43,44], barriers of about 10.5  $\pm$ 1.5, 9.7  $\pm$  1.5, 8.4  $\pm$  1.5, and 7.7  $\pm$  1.5 are then

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estimated for the four species. These barriers are comparable with data obtained in theoretical treatments. Ferenac et al. [14] estimated a barrier height of 8– 12 kcal/mole for the methyl acetate system, whereas Rayez et al. [13] reported a barrier of 6.5 kcal/mole for ethyl acetate, a little lower than what is implied by our data. A theoretical treatment of HC(O)OCH(O<sup>•</sup>)CH<sub>3</sub> has also been conducted as part of our recent study [38] of isopropyl and *t*-butyl formate oxidation. In that work, the  $\alpha$ -ester rearrangement reaction (9) and decomposition reaction (11) were found to be competitive, with the  $\alpha$ -ester process possessing an activation barrier of 12 kcal/mole, somewhat higher than measured here.

#### SUMMARY

Rates of the  $\alpha$ -ester rearrangement reaction have been determined for the HC(O)OCH(O<sup>•</sup>)CH<sub>3</sub> and CH<sub>3</sub>C(O)OCH(O<sup>•</sup>)CH<sub>3</sub> alkoxy species, relative to the reaction of these radicals with O<sub>2</sub>. For both species, the rearrangement reaction is found to dominate over reaction with O<sub>2</sub> in air at 1 atm and 298 K and to be competitive with reaction with O<sub>2</sub> near 250 K. Barriers to the rearrangement reaction of  $8.4 \pm 1.5$  and 7.7  $\pm$  1.5 kcal/mole are estimated for the two radicals. In considering data for the four structurally similar radicals (this work and [15]), RC(O)OCH(O<sup>•</sup>)R', R, R' = H, CH<sub>3</sub>, it is seen that the rates of the rearrangement reaction near 298 K increase by a factor of approximately 3–4 upon substitution of R = CH<sub>3</sub> for R = H and a factor of approximately 30 upon substitution of R' = CH<sub>3</sub> for R' = H, corresponding to a decreases in the barrier height of approximately 1 and 2 kcal/mole, respectively.

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