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Temperature Dependence of the Alpha-Ester Rearrangement Reaction

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Measurements have been made of the oxidation products of methyl formate and methyl acetate as a function of temperature (253−324 K). Both processes show the occurrence of the α-ester rearrangement channel $RC(O)OCH_2O^\bullet \rightarrow RC(O)OH + HCO$, which has an activation energy of ∼10 kcal mol^{-1}. Reaction of hydroxyl radicals with methyl formate occurs with roughly equal efficiency at both of the carbon atoms, while OH-reaction with methyl acetate leads to 30−40% attack at the acetate group.

Introduction

The atmosphere contains a rich suite of oxygenated organic compounds, which can be either emitted directly or formed by in situ oxidation of primary emissions.[1] Esters are potential oxygenated atmospheric constituents. While esters are naturally occurring compounds in fruits and flowers, their main source in the atmosphere probably comes from their use as solvents in paints, adhesives, and cleaning agents, and from the food industry. The use of esters as solvents is attractive, since they appear to have low ozone creation potentials.[2] Esters may also be produced in the atmospheric oxidation of ethers.[3,4] Methyl formate has a potentially significant source from the use of linear methyl ethers CH_3OR and in particular dimethyl ether which has been proposed as an additive in diesel fuel. Methyl acetate, on the other hand, is a common product from branched methyl ethers such as methyl *tert*-butyl ether and methyl *tert*-amyl ether which have been used as gasoline additives. Few (if any) measurements of esters in the atmosphere have been published, although methyl acetate has recently been tentatively identified in the atmosphere in Houston, Texas (E. Atlas, University of Miami, personal communication, 2003). Methyl acetate and methyl formate, the two simplest esters, have relatively long atmospheric lifetimes, since they react slowly with OH radicals[5−10] and are not expected to be subject to photolysis.[11]

$$OH + CH_3C(O)OCH_3 \rightarrow \text{products}$$
$$k_1 = 3.5 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (1)$$

$$OH + HC(O)OCH_3 \rightarrow \text{products}$$
$$k_2 = 1.8 \times 10^{-13}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1} \quad (2)$$

The position of attack by OH has not been determined experimentally for either molecule, and estimates of the selectivity using either structure−activity relationships[6,8,10] or theoretical calculations for methyl formate[9,10] are not conclusive.

Mechanistic studies of both methyl formate and methyl acetate have been published in the past few years, and both oxidations involve the α-ester rearrangement reaction, first reported by Tuazon et al. in 1998.[12]

$$CH_3C(O)OCH_2O^\bullet \rightarrow CH_3C(O)OH + HCO \quad (3)$$

$$HC(O)OCH_2O^\bullet \rightarrow HC(O)OH + HCO \quad (4)$$

For both molecules, the ester rearrangement is slow enough to allow competition with the O_2 reaction, and so valuable kinetic information can be obtained by measuring relative product yields as a function of oxygen partial pressure.[13−15]

$$CH_3C(O)OCH_2O^\bullet + O_2 \rightarrow CH_3C(O)OCHO + HO_2 \quad (5)$$

$$HC(O)OCH_2O^\bullet + O_2 \rightarrow HC(O)OCHO + HO_2 \quad (6)$$

The α-ester rearrangement reaction is rather unusual in that it involves a five-membered H-atom transfer to the oxygen atom of the carbonyl group. Currently, the dynamics of this reaction are not well understood. Three papers have addressed the energetics of the transition state theoretically, although the high degree of delocalization of the transition state makes calculation difficult.[16−18] In an attempt to obtain a better understanding of these reactions, we have conducted a study of the products of the oxidation of methyl acetate and methyl formate as a function of O_2 partial pressure and temperature. Product studies were carried out using chlorine atoms to initiate the reaction. The results lead to an estimate of the activation energy for the α-ester rearrangement, which will allow for a better constraint on theoretical estimates. The mechanism of the reaction of OH radicals with methyl formate and methyl acetate was also studied at room temperature.

Experimental Section

The experiments were all conducted in a 47-L stainless steel chamber.[14,19] Chilled ethanol was circulated through the outer jacket to reach temperatures below 296 K, or heated water could be circulated for higher temperatures. Gas mixtures were analyzed via FTIR spectroscopy using a resolution of 1 cm^{-1}. Standard spectra obtained in-house were used, except for formic anhydride (FAN) and acetic formic anhydride (AFAN), the room-temperature spectra of which were provided digitally by Dr. T. Wallington at Ford Motor Company. Whenever possible, standards were taken at the appropriate temperatures for the

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experiments. For FAN and AFAN, product spectra obtained at temperatures other than 296 K were calibrated against the room-temperature standard spectra using integrated band strengths. Concentrations of formic and acetic acid (AcOH) were corrected for the presence of dimers using the equilibrium constants given by Dagaut et al.[20] The corrections were applied both to the amounts of acid in the calibration bulb (at 296 K) and the products formed in the reaction chamber (most important at the lowest temperature studied). Calibration curves were used for CO and CO_2 to account for curvature caused by saturation of the lines at the concentrations used. Absolute concentration measurements at 296 K are considered to be accurate to better than 5%. At other temperatures, the uncertainty is expected to be a little higher (7−8%).

Irradiation of gas mixtures was via a xenon arc lamp, filtered to give output from 250 to 420 nm. The majority of the experiments involved the photolysis of Cl_2 in the presence of methyl formate (MF) or methyl acetate (MeAc), with various partial pressures of O_2 (6−600 Torr), in a total of 700 Torr (balance N_2). Mixtures were photolyzed for several periods of up to 5 min, and IR spectra were taken initially and after each successive irradiation. Typical concentrations (molecule cm^{-3}) used were ester $(3-4) \times 10^{14}$, Cl_2 $(7-12) \times 10^{14}$, NO when used 7×10^{14}. At the lower temperatures, where reduced pressures of O_2 were required, the Cl_2 concentration was reduced to maintain a ratio $[O_2]/[Cl_2] > 100$, thus avoiding loss of alkyl radicals to reaction with Cl_2. Further experiments were done at 253 K using reduced total pressure or with NO present to test whether chemical activation of the oxy radicals could affect the product distribution.

The mechanisms of the reactions of OH with methyl formate and methyl acetate were also investigated at 296 K. For these experiments, methyl nitrite $(1.5-2.1) \times 10^{15}$ molecule cm^{-3} was photolyzed in the presence of NO $(2.8-4.1) \times 10^{14}$ molecule cm^{-3} and methyl formate 7×10^{15} molecule cm^{-3} or methyl acetate $(2.1-3.5) \times 10^{15}$ molecule cm^{-3} in the presence of 60−540 Torr O_2 at 700 Torr total pressure. The duration of the irradiation periods was ∼10 min. As a consequence of the slow rates of the OH reactions, high concentrations of the esters had to be used, making measurement of the consumption of starting material unreliable. Hence, in several experiments a small amount (1.5×10^{14} molecule cm^{-3}) of C_2H_4 was added as a tracer, and the consumption of ester was calculated from the measured loss of C_2H_4.

$$OH + C_2H_4 \rightarrow HOCH_2CH_2^{\bullet} \tag{7}$$

The loss can be expressed in terms of the relative rates. Assuming a small extent of conversion for the ester (i.e., $\ln(1 - x) \sim -x$), results, for methyl formate, in equation E1.

$$\Delta MF \approx [MF]_0 \times \frac{k_2}{k_7} \ln\left(\frac{[C_2H_4]_0}{[C_2H_4]_t}\right) \tag{E1}$$

The rate coefficient for the reaction of OH with ethene is well-known,[21] $k_7 = (7.9 \pm 0.4) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}, and ethene has convenient, sharp infrared features that enable its loss to be measured accurately in the presence of large concentrations of the esters.

Results

The oxidation mechanisms of methyl formate and methyl acetate have previously been studied at 296 K.[13,14] Experiments were first conducted at room temperature to confirm the previous results before studying the mechanisms in more detail at temperatures of 253, 273, and 324 K.

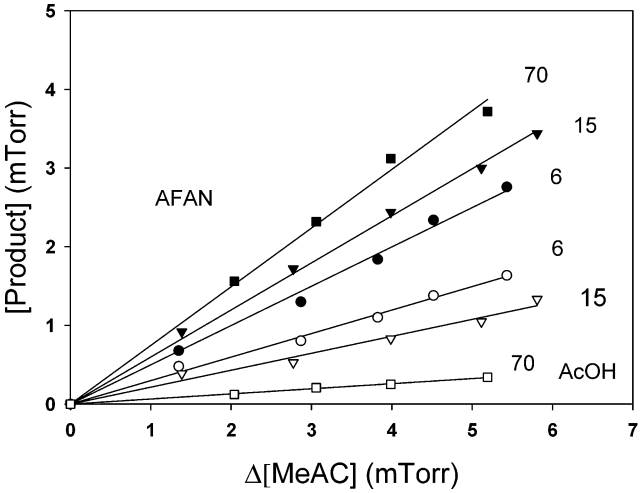

Figure 1. Production of acetic formic anhydride (AFAN; filled symbols) and acetic acid (AcOH; open symbols) as a function of methyl acetate loss due to reaction with chlorine atoms at 253 K. Circles, 6 Torr O_2; triangles, 15 Torr O_2; squares, 70 Torr O_2. The acetic acid concentrations have been corrected for equilibration with the dimer.

Methyl Acetate Oxidation. Methyl acetate was stable in the chamber, with a wall-loss rate in the dark of less than 10^{-6} s^{-1}. The experiments were carried out in the absence of NO, since at low temperatures the formation of nitrates complicates the product yields and also slows down the rate of conversion. Reaction of chlorine atoms with methyl acetate is thought to result only in abstraction at the methoxy group, leading to production of $CH_3C(O)OCH_2O_2$ radicals.[13] These peroxy radicals react to give either oxy radicals, or molecular products.

$$CH_3C(O)OCH_2O_2 + CH_3C(O)OCH_2O_2 \rightarrow CH_3C(O)OCH_2O^{\bullet} + CH_3C(O)OCH_2O^{\bullet} + O_2 \tag{8a}$$

$$CH_3C(O)OCH_2O_2 + CH_3C(O)OCH_2O_2 \rightarrow CH_3C(O)OCHO + CH_3C(O)OCH_2OH + O_2 \tag{8b}$$

The oxy radicals either decompose by the α-ester rearrangements or react with O_2 to give acetic formic anhydride (AFAN).

$$CH_3C(O)OCH_2O^{\bullet} \rightarrow CH_3C(O)OH + HCO \tag{3}$$

$$CH_3C(O)OCH_2O^{\bullet} + O_2 \rightarrow CH_3C(O)OCHO + HO_2 \tag{5}$$

Yields of AFAN and acetic acid were measured as a function of the partial pressure of O_2 at each temperature studied. Figure 1 shows the formation of acetic acid and AFAN at several different oxygen partial pressures at 253 K, while Figure 2 shows the same for 324 K. The slopes of these plots give the corresponding yields. The product yields from methyl acetate measured in this work are shown in Figure 3. The acetic acid has been corrected for formation of dimer at 253 K; at higher temperatures the correction was negligible. The maximum correction to the concentration was 30%, at the lowest O_2 (2 Torr); this led to a 20% change in the slope at that oxygen pressure. However, the effect on the value of k_5/k_3 is less than 10%, even if the dimer is totally ignored. The sum of the yields of acetic acid and AFAN was independent of O_2 at a given temperature and were typically 75−80%. The remainder is thought to be either the alcohol from 8b or hydroperoxides formed in the reaction of the peroxy radicals with HO_2. The

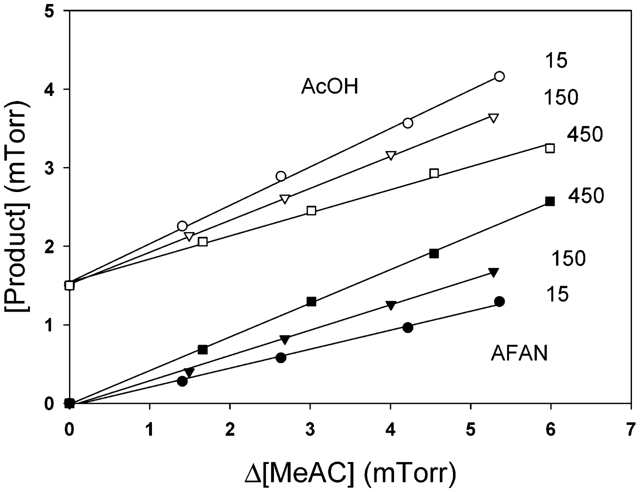

Figure 2. Same as Figure 1, except at 324 K. The data for acetic acid have been moved upward by 1.5 mTorr for clarity. Circles, 15 Torr O_2; triangles, 150 Torr O_2; squares, 450 Torr O_2.

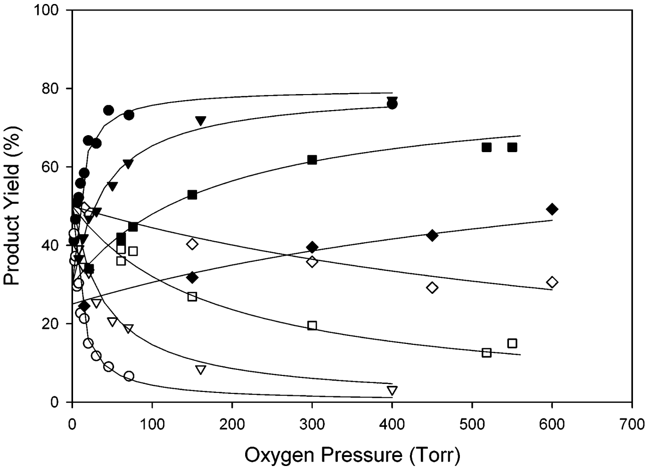

Figure 3. Plot of product yields from the oxidation of methyl acetate by chlorine atoms as a function of oxygen pressure as a function of temperature. Circles, 253 K; triangles, 273 K; squares, 296 K; diamonds, 324 K. Acetic formic anhydride is given by closed symbols, acetic acid by open ones. The lines are a simultaneous fit to all the data using equations E2 and E3, with a difference in activation energies ΔE of 9.6 kcal mol^{-1}.

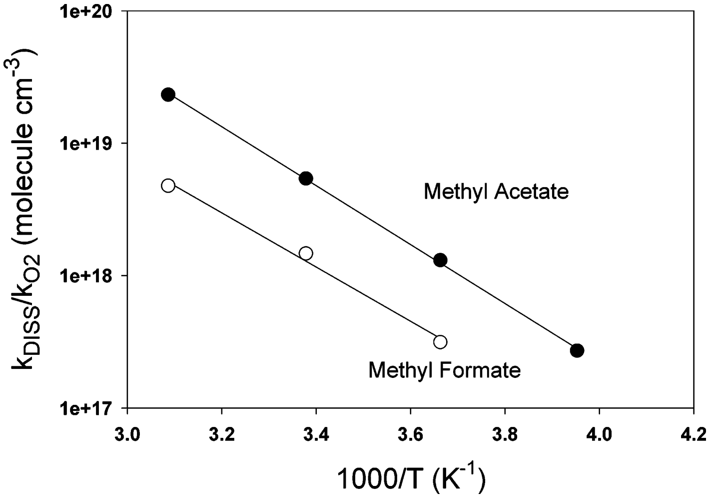

Figure 4. Arrhenius plot for the rate coefficients ratios k_3/k_5 and k_4/k_6 for the α-ester rearrangements of methyl acetate and methyl formate.

occurrence of the molecular channel 8b of the self-reaction of the $CH_3C(O)OCH_2O_2$ radicals leads to a production of AFAN independent of the O_2 concentration, resulting in the intercept in Figure 3. The reactions of alcohols and peroxides with chlorine atoms are expected to be more rapid than that of the starting material, and probably give AFAN as a product, which may also contribute to the intercept in the AFAN yield in Figure 3.

Yields of CO and CO_2 were also measured. The oxygen dependence of the CO yield paralleled that of acetic acid, but its yield lay about 10% higher (an effect also noted by Christensen et al.[13]). The CO_2 yield was independent of O_2 and was in the range 8−10%, with indications of upward curvature at longer reaction times. Thus, it is possible that a single channel exists leading to the formation of both CO and CO_2, since the "excess" CO is roughly equal to the CO_2. It is possible that both these compounds form in the reaction of Cl atoms with one of the primary products, resulting in curvature in the CO_2 plots, which is not observed in the CO yield because of the strong primary source of CO. Christensen et al.[13] noted the formation of an unknown product which absorbs near 1030 cm^{-1} and is consumed rapidly by Cl atoms. We also observed this product. The infrared features correspond closely to those of $CH_3C(O)OCH_2OOH$, reported by Neeb et al.[22] It may be the source of the extra CO and CO_2 seen, although the oxidation of $CH_3C(O)OCH_2OOH$ is more likely to give AFAN as a product than CO or CO_2. Thus, at present the identity of this product remains unknown.

Assuming that the yield of AFAN which did not come from oxy radicals was independent of oxygen, the O_2 dependence of the yields Y_{AcOH} and Y_{AFAN} can be given by the following expressions, where Y_{RAD} is the yield of the alkoxy radical, and INT the O_2-independent intercept.

$$Y_{AcOH} = Y_{RAD} \times \left(1 + \frac{k_5}{k_3}[O_2]\right)^{-1} \tag{E2}$$

$$Y_{AFAN} = INT + Y_{RAD} \times k_5[O_2](k_3 + k_5[O_2])^{-1} \tag{E3}$$

The room-temperature data, $k_3/k_5 = (5.4 \pm 0.6) \times 10^{18}$ molecule cm^{-3} (2-σ precision), agree very well with those of Christensen et al., $(6.0 \pm 2.4) \times 10^{18}$ molecule cm^{-3}.[13] To obtain an activation energy for the decomposition reaction, all the data were fit simultaneously to equations E2 and E3. The room-temperature value of k_3/k_5 was fixed to the average of our and Christensen's values, and the difference in the activation energies, ΔE, was optimized until the best fit to all the data was obtained. The resulting fits are shown in Figure 3. In fitting the data, the intercepts in the AFAN yields were taken directly from the measured yields at the lowest O_2 pressures. As can be seen, all the data can be fitted simultaneously, using a value of $\Delta E = (9.6 \pm 1.0)$ kcal mol^{-1}. Reactions of oxy radicals with O_2 such as reaction 5 usually have an activation energy in the range 0.5−1.0 kcal mol^{-1}, suggesting that the activation energy for the decomposition channel is in the range 9.1−11.6 kcal mol^{-1}, with a most probable value of 10.1 kcal mol^{-1}. Figure 4 shows the ratios k_3/k_5 in Arrhenius form derived by fitting the data with equations E2 and E3 individually at each temperature, and the results are also summarized in Table 1. Although the precision on a given fit is about 10%, the uncertainty is reduced by simultaneously fitting both the CH_3COOH and AFAN. Including calibration uncertainties, we estimate the overall uncertainty to be about 12% at room temperature, increasing to 15% at the extreme temperatures as a result of the increased uncertainties in calibration.

Christensen et al.[13] also did experiments at 296 K in the presence of NO, finding that the yield of the decomposition

TABLE 1: Ratio of Rate Coefficients for Dissociation versus Reaction with O_2 at Various Temperatures for Methyl Acetate (k_3/k_5) and Methyl Formate (k_4/k_6)[a]

	temperature (K)			
	253	273	296	324
k_3/k_5	$(2.7 \pm 0.4)\ 10^{17}$	$(1.3 \pm 0.2)\ 10^{18}$	$(5.4 \pm 0.7)\ 10^{18}$	$(2.3 \pm 0.3)\ 10^{19}$
k_4/k_6		$(3.1 \pm 0.4)\ 10^{17}$	$(1.5 \pm 0.2)\ 10^{18}$	$(4.8 \pm 0.7)\ 10^{18}$

[a] The ratios have units of molecule cm^{-3}.

product, $CH_3C(O)OH$, was higher when NO was present. From an analysis of the product yields as a function of O_2 pressure, they deduced that chemical activation of the oxy radical $CH_3C(O)OCH_2O^{\bullet}$ was occurring about 20% of the time. We conducted an experiment in the presence of NO at 253 K to explore the possibility that chemical activation of $CH_3C(O)OCH_2O^{\bullet}$ radicals could enhance the production of acetic acid. The experiment used 70 Torr O_2, which is sufficient to suppress the decomposition of thermalized radicals at that temperature. The analysis of the experiment was complicated by the formation of peroxynitrates, RO_2NO_2, in reaction 9, which reduced the overall yield of AFAN + CH_3COOH.

$$CH_3C(O)OCH_2O_2 + NO_2 + M \rightarrow CH_3C(O)OCH_2O_2NO_2 + M \quad (9)$$

However, the ratio $[CH_3COOH]/[AFAN]$ should still be a good indicator of the relative yields. In the absence of NO, the ratio $[CH_3COOH]/[AFAN]$ was 1/11, but increased to 1/4 in the presence of NO, indicating clearly that activation was occurring at 253 K. This is consistent with the 20% yield of chemically activated radicals found by Christensen at 296 K.

Experiments were conducted at 296 and 273 K at reduced pressure to see whether a pressure dependence related to the alpha-ester rearrangement could be discerned. These experiments were done at 120 Torr total pressure using 60 Torr O_2 at 296 K and 14 Torr O_2 at 273 K and were compared to experiments containing the same amount of O_2 at 700 Torr total pressure. No difference in product yields could be found compared to the experiments at 700 Torr, indicating that the ester rearrangement does not depend strongly on pressure, assuming that the other reactions leading to these products are also independent of pressure.

Three experiments were performed to investigate the reaction of OH with methyl acetate. Oxygen pressures of 140 and 300 Torr were used, with methyl acetate concentrations in the range $(2.1-3.5) \times 10^{15}$ molecule cm^{-3}. The presence of NO was unavoidable in these experiments, since it is used to generate OH radical. Ethene was used as a tracer to calculate the methyl acetate loss, as described in the Experimental Section by equation E1. There is good agreement between the three measurements of k_1,[5-7] and the average value 3.5×10^{-13} cm^3 molecule^{-1} s^{-1} was used. The product distributions were qualitatively different from those obtained using Cl atoms. The sum of CH_3COOH and AFAN was only 50% and a large yield of CO_2 was observed, approaching 60%. Upon closer inspection, the CO_2 behaved like a secondary product and appeared after an initial delay. Since very low yields of CO_2 are obtained with Cl atoms, which only react at the methoxy group, it is concluded that OH attack also occurs at the acetyl group. The large secondary yield of CO_2 is consistent with production, and subsequent loss, of methyl glyoxylate, $HC(O)C(O)OCH_3$, from the oxy radical formed at the acetyl group.

$$^{\bullet}OCH_2C(O)OCH_3 + O_2 \rightarrow HO_2 + HC(O)C(O)OCH_3 \quad (10)$$

Cavalli et al. observed the formation of methyl glyoxylate in high yield from the photolysis of methyl bromoacetate.[23] The observation that the $^{\bullet}OCH_2C(O)OCH_3$ radical reacts with oxygen rather than decomposing is expected from the thermochemistry for that radical.[18] Loss of methyl glyoxylate could occur through reaction with OH radicals, leading to the production of two CO_2 molecules.

$$OH + HC(O)C(O)OCH_3 \rightarrow H_2O + {}^{\bullet}C(O)C(O)OCH_3 \quad (11)$$

$$^{\bullet}C(O)C(O)OCH_3 + O_2 \rightarrow O_2C(O)C(O)OCH_3 \quad (12)$$

$$O_2C(O)C(O)OCH_3 + NO \rightarrow\rightarrow CO_2 + CO_2 + HCHO \quad (13)$$

It is also feasible that the $^{\bullet}C(O)C(O)OCH_3$ radical decomposes to $CO + CH_3OCO$, which oxidizes to give $CO + CO_2$.[14] Methyl glyoxylate could also be lost by photolysis, to give $HCO + CH_3OCO$. The overall impact of these reactions would be to produce one CO_2 per molecule lost.

Figure 5 shows the formation of products as a function of methyl acetate loss. The CO_2 yields are consistent with 35−40% attack at the $CH_3C(O)$ group leading to two molecules of CO_2. Under the conditions of the experiment, the steady-state concentration of the methyl glyoxylate would only be $\sim 1 \times 10^{13}$ molecule cm^{-3}, and since most of the bands reported by Cavalli et al.[23] would be obscured by the starting material, quantification of this product would be impossible. In the absence of further information regarding the fate of methyl glyoxylate, further analysis of the CO_2 yield is not warranted.

Methyl Formate Oxidation. As detailed in previous studies,[14,15] CO, CO_2, FAN, and formic acid are all observed in the oxidation of methyl formate. Formic acid, CO, and FAN are from abstraction at the methyl group, while HCHO and CO_2 are produced following abstraction of the formyl hydrogen.

$$HC(O)OCH_2O_2 + HC(O)OCH_2O_2 \rightarrow HC(O)OCH_2O^{\bullet} + HC(O)OCH_2O^{\bullet} + O_2 \quad (14)$$

$$HC(O)OCH_2O^{\bullet} \rightarrow HC(O)OH + HCO \quad (4)$$

$$HC(O)OCH_2O^{\bullet} + O_2 \rightarrow HC(O)OCHO + HO_2 \quad (6)$$

$$HCO + O_2 \rightarrow HO_2 + CO \quad (15)$$

$$CH_3OC(O)O_2 + CH_3OC(O)O_2 \rightarrow CH_3OC(O)O^{\bullet} + CH_3OC(O)O^{\bullet} + O_2 \quad (16)$$

$$CH_3OC(O)O^{\bullet} \rightarrow CH_3O + CO_2 \quad (17)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \quad (18)$$

As a result of the slow rate of reaction of methyl formate with Cl atoms,[24] HCHO is rapidly removed by Cl atoms to form CO.

$$Cl + HCHO \rightarrow HCl + HCO \quad (19)$$

Since decomposition of the $HC(O)OCH_2O^{\bullet}$ radical is competitive with the O_2 reaction, the yields of CO, HC(O)OH, and FAN should be oxygen-dependent, while that of CO_2 is expected to be constant.[14] The yields of formic acid and formic anhydride were fitted with equations analogous to E2 and E3 at each temperature. Product yields are shown in Figure 6 for the experiments at 324 K. The expected dependence on O_2 is found,

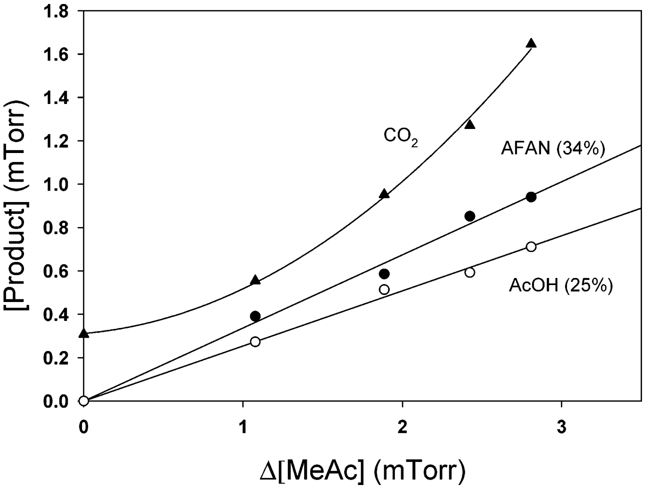

Figure 5. Product yields from the reaction of OH with methyl acetate in 300 Torr O_2. Initial conditions: MeAc, 66 mTorr; CH_3ONO, 43 mTorr; NO, 13 mTorr; C_2H_4, 2.7 mTorr. The data for CO_2 have been offset vertically by 0.3 mTorr, and the line through the CO_2 data is a quadratic fit, for visual purposes.

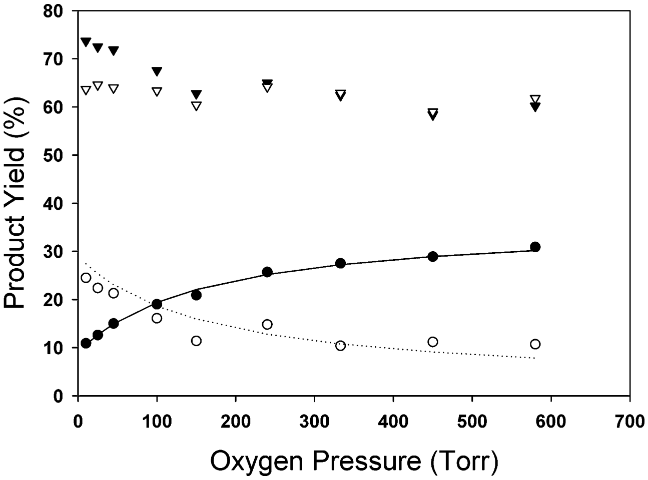

Figure 6. Yields of products as a function of partial pressure of O_2 from the OH-oxidation of methyl formate at 324 K. Open circles, formic acid; closed circles, formic anhydride; open triangles, CO_2; closed triangles, CO. The lines represent a simultaneous fit to the data using a value $k_4/k_6 = 4.8 \times 10^{18}$ molecule cm^{-3}.

and the data can be fitted with a value for k_4/k_6 of $(4.8 \pm 0.5) \times 10^{18}$ molecule cm^{-3}. Values of k_4/k_6 obtained at different temperatures are given in Table 1 and shown in Figure 4. The magnitudes of the uncertainties are similar to those for methyl acetate, 12−15% depending on temperature. The branching ratio for abstraction by Cl atoms does not appear to have a particularly strong temperature dependence, since the combined yield of formic acid and formic anhydride only varies from 45% at 273 K to 37% at 324 K.

In our previous study, we reported the presence of an absorption feature at 1308 cm^{-1},[14] and tentatively suggested that this product came from abstraction at the H−C(O) group, possibly the ester monomethyl carbonate $CH_3OC(O)OH$. The presence of this band was noted at all the temperatures studied. The absence of a similar feature in the methyl acetate experiments supports the tentative assignment.

At 253 K, the decomposition of the oxy radical (reaction 4) was sufficiently slow that no dependence of the product yields on O_2 was found. Yields of 41% and 5% were obtained for the FAN and HCOOH, respectively. The source of HCOOH is uncertain, but may be the reaction of HO_2 with HCHO, which is more efficient at low temperature. Wall effects may also play a role at low temperature. An extrapolation of the results obtained at higher temperature gives a ratio k_4/k_6 which is equivalent to 1.6 Torr O_2 at 253 K, so little dependence is expected for 10 Torr O_2 and above. An experiment was done in air at 253 K in the presence of NO to look for the occurrence of chemical activation. The yields of FAN (22%) and HCOOH (3%) were both reduced from what was found in the absence of NO, because of the formation of nitrates and peroxynitrates.[14,25] Because of the difficulty in measuring and interpreting the low yields of HCOOH, along with the reduced total yields, no firm conclusions can be reached regarding the occurrence of chemical activation in this experiment.

Products from the OH-initiated reaction of methyl formate were compared with those from the Cl reaction at 296 K, to ascertain the relative rates of attack at the two carbon atoms. Ethene was again included in the mixtures as a tracer. Measurements of rate coefficients for reaction 2 at 296 K range from 1.7×10^{-13} in ref 8 to 2.3×10^{-13} cm^3 $molecule^{-1}$ s^{-1} in ref 7, although the most recent measurements[8−10] agree to within a few percent. Thus, we used a rate coefficient of 1.8×10^{-13} cm^3 $molecule^{-1}$ s^{-1} to calculate the loss. The product yields could also be normalized relative to the sum of the major products and compared to the calculated loss of methyl formate when C_2H_4 was present. This reduces any uncertainties associated with the rate coefficient for OH with methyl formate. Products identified were HCOOH, HC(O)OCHO, and CO_2. CO was also observed, but it was not quantified, since it is also produced by oxidation of HCHO formed from OH + ethene and from methyl nitrite photolysis. Toward the end of the reaction, the PAN-analogue $CH_3OC(O)OONO_2$ was also apparent in the spectra.[14,25] Figure 7 shows part of the spectrum from an experiment with 300 Torr O_2. Since a large part of the spectrum is saturated, only certain windows could be used for analysis. Nevertheless, the production of FAN and HCOOH can clearly be seen on the wing of the large MF absorption near 1100 cm^{-1}.

Clear evidence was found for abstraction at each end of the molecule by OH. Formic acid and acetic formic anhydride result from abstraction at the methyl group, while CO_2 and the PAN analogue are indicative of abstraction at the acyl group.[14] A series of runs was performed in which the oxygen partial pressure was varied from 60 to 300 Torr. Typical data are shown for an experiment in air (140 Torr O_2) in Figure 8, normalized to the sum of the measured products (which was 109% for that run). Product yields for all the experiments are summarized in Table 2. The measured branching ratios for abstraction varied from 60:40 to 40:60. Taking into account the occurrence of chemical activation at 296 K, the product distributions from OH and Cl were essentially identical, indicating that OH radicals abstract with roughly equal efficiency from the H−C(O) and $-CH_3$ groups in methyl formate.

Discussion

The α-ester rearrangement was first discovered in 1998 and has not yet been the subject of a large number of studies. Tuazon et al. first demonstrated its occurrence for the oxidation of ethyl acetate.[12] Since then, there have been further studies of ethyl, isopropyl, and isobutyl acetates in air,[26,27] along with investigations of the oxidation of methyl acetate,[13] methyl propionate,[23] and methyl formate[14] which used varying oxygen pressures. However, all these studies were done at room temperature and do not give any information about the thermochemical parameters for the reaction.

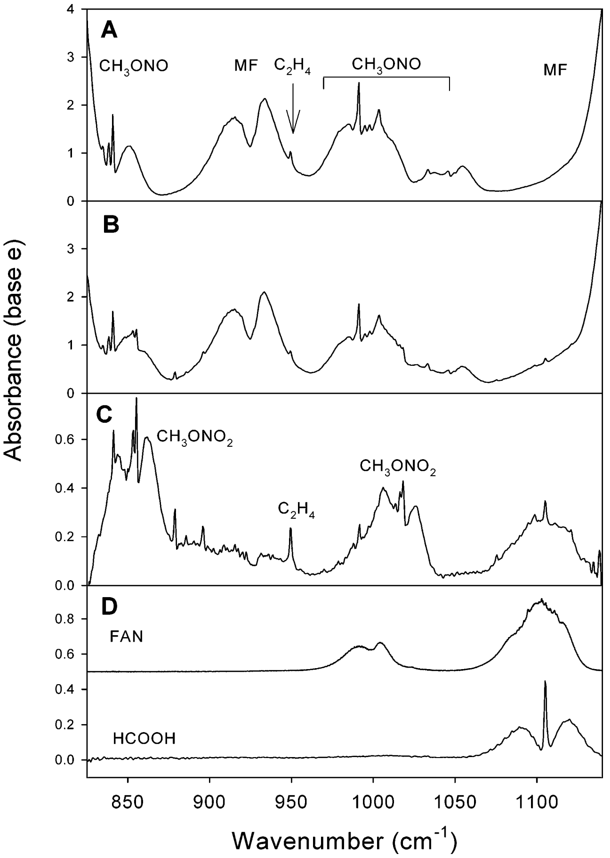

Figure 7. Sequence of spectra showing the oxidation of methyl formate by OH radicals in the presence of 300 Torr O_2. Initial concentrations were MF (6.95×10^{15}), CH_3ONO (2.1×10^{15}), ethene (1.3×10^{14}), and NO (5.5×10^{14} molecule cm^{-3}). A: starting mixture; B: spectrum after 36 min photolysis; C: residual spectrum after subtraction of MF and CH_3ONO; D: reference spectra of HCOOH (7.5×10^{13}) and formic anhydride (6.1×10^{13} molecule cm^{-3}).

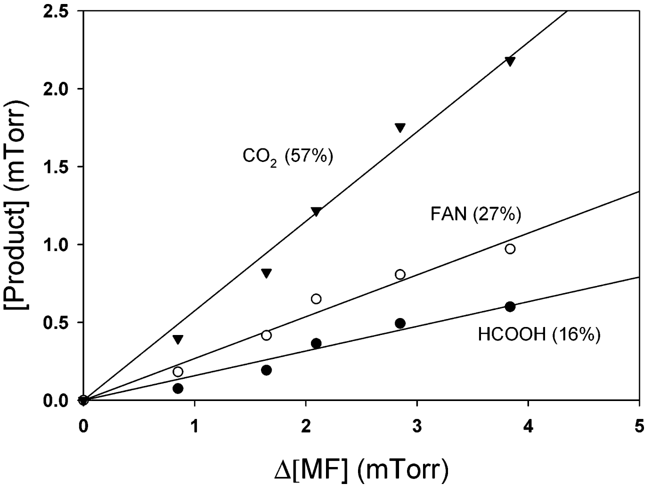

Figure 8. Product distribution from the reaction of OH radicals with methyl formate at 296 K in air. The yields have been normalized to 100%, to account for difficulties in quantifying the loss of methyl formate. Initial conditions: methyl formate, 217 mTorr; methyl nitrite, 66 mTorr; ethene, 4 mTorr; NO, 13 mTorr. Yields are shown for CO_2, formic acid anhydride (FAN), and formic acid (HCOOH).

The present study is the first to investigate the temperature dependence of the ester rearrangement and as such offers information on the activation energy. As seen in Figure 4, the activation energies for methyl acetate and methyl formate are identical, within experimental uncertainties, although the decomposition reaction for methyl acetate is faster relative to the O_2-reaction. It is not clear whether this difference represents a small difference in the activation energy, the A-factor, or both. The measured activation energy is about 10−11 kcal mol^{-1}. This is consistent with the observation of a limited degree of chemical activation,[4,28] since the available energy from the reaction $RO_2 + NO$ is typically around 10 kcal mol^{-1}.

TABLE 2: Percentage Product Yields for the Reaction of Hydroxyl Radicals with Methyl Formate as a Function of Oxygen Partial Pressure at 296 K[a]

$P(O_2)$	HCOOH	FAN	HCOOH + FAN	CO_2 + PAN
60	29 (24)	25 (20)	54 (44)	69 (56)
140	18 (16)	29 (27)	47 (43)	62 (57)
300	19 (16)	43 (36)	62 (51)	59 (49)

[a] Yields in parentheses have been normalized to the total of measurable products.

Calculations on the energetics of the α-ester rearrangement were made by Good and Francisco,[16] Rayez et al.,[17] and Ferenac et al.[18] Good and Francisco calculated a barrier of about 13 kcal mol^{-1} for the methyl formate radical, a little larger than what was measured here. Rayez found a relatively low barrier for ethyl acetate, 6−7 kcal mol^{-1}. The larger E_a of 10.1 kcal mol^{-1} reported herein is consistent with the slower rate coefficients for the radicals studied (ethyl acetate undergoes 100% decomposition, methyl acetate and methyl formate competitive decomposition, and O_2 reaction at 296 K). Rayez et al. also calculated the rate coefficient as a function of pressure using RRKM theory. At 296 K, the rate coefficient was predicted to be in the falloff region at atmospheric pressure (roughly a factor of 2 below the high-pressure limit) with a value of 3.7×10^7 s^{-1}. The high-pressure A-factor was calculated as 4.7×10^{12} s^{-1}. The current experiments did not show any pressure dependence for the reaction of methyl acetate. Assuming a rate coefficient for k_5 of 8×10^{-15} cm^3 $molecule^{-1}$ s^{-1} gives a room-temperature rate coefficient of 4.6×10^4 s^{-1} and an A-factor at 1 atm of 4.2×10^{12} s^{-1}, on the basis of the activation energy measured here. The reaction is about 3 orders of magnitude slower than that estimated for ethyl acetate, although the A-factor is very similar.

Ferenac et al.[18] found that the barrier to dissociation of $CH_3C(O)OCH_2O^{\bullet}$ was very sensitive to the level of theory used, obtaining 7−8 kcal mol^{-1} with B3LYP and ∼11 kcal mol^{-1} with G2(MP2). The latter result is clearly in better agreement with the experimental results obtained in the present work. Ferenac et al. also pointed out that tunneling may make a small contribution to the reaction rate (∼30%) and so the measured barrier could be lower than the true one by up to 1 kcal mol^{-1}, which would bring the experimental and calculated results into very good agreement.

The present study also indicates that both chlorine atoms and OH radicals abstract from the two different carbon atoms in methyl formate with roughly equal rates. The structure additivity relationships (SAR) of Le Calvé et al.[8] also indicate that the branching ratio for OH should be 50:50. However, further conclusions from that paper (and also experimental results from our laboratory on isopropyl and *tert*-butyl formates) indicate that strict group additivity cannot be used in calculating the rate coefficients for larger formates and that caution should be exercised in making these extrapolations. Good et al.[9] made ab initio calculations of the reaction thermochemistry and activation barriers and implied that abstraction by OH from both ends of the molecule should occur, with an overall rate coefficient very similar to that measured. However, their calculations suggested that the majority of the reaction (86%) should occur at the

H−C(O) group, although such calculations are clearly very sensitive to the magnitudes of the barriers (which were both less than 5 kcal mol^{-1}) and the extent of tunneling. For comparison, the local activation energy measured at 296 K by Le Calvé et al. was only 0.9 kcal mol^{-1}, which is probably lower than the uncertainty in the thermochemical parameters involved. We also demonstrate that OH attacks methyl acetate at both carbon atoms, with up to 40% occurring at the acetyl group. This is again consistent with the structure−activity relationship developed by Mellouki and co-workers.[6,8] Szilágyi et al. recently attempted to express the SAR in terms of the groups HC(O)O− and $CH_3C(O)O-$, rather than modifying the rates for carbonyl groups.[10] While their predicted rate coefficients are reasonable, the method is not successful in predicting the branching ratio found here for methyl formate with OH.

The present study enables the atmospheric fate of methyl formate and methyl acetate to be predicted over a range of conditions. It is not expected that the relative fractions of abstraction by OH will vary strongly with temperature, because of the low overall barrier to reaction. The branching of the acyloxy-substituted methoxy radicals should be described well by the temperature-dependent decomposition rates reported here. In methyl formate, approximately half of the reaction occurs at the formyl group. While the reactions of the oxy radical $CH_3OC(O)O^\bullet$ probably do not depend strongly on temperature (with rapid decomposition dominating), the potential for formation of the PAN-analogue $CH_3OC(O)O_2NO_2$ will of course depend on the ratio NO:NO_2, and the thermal stability of the PAN-analogue will also be temperature dependent. Interestingly, this PAN-analogue may have been tentatively identified in ambient air using chemical ionization mass spectrometry (F. Flocke, NCAR, personal communication). For methyl acetate, abstraction at the acetyl group will probably lead to the formation of methyl glyoxylate, which could react with OH, photolyze, or be removed by aqueous particles.

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