Atmospheric Chemistry of Dimethoxymethane ($CH_3OCH_2OCH_3$): Kinetics and Mechanism of Its Reaction with OH Radicals and Fate of the Alkoxy Radicals $CH_3OCHO(\bullet)OCH_3$ and $CH_3OCH_2OCH_2O(\bullet)$

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The rate constant for the reaction of dimethoxymethane (DMM) with OH radicals was determined to be $(4.6 \pm 1.6) \times 10^{-12}$ at 346 ± 3 K using a pulse radiolysis/transient UV absorption absolute rate technique and $(5.3 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 295 ± 2 K using an FTIR-smog chamber relative rate technique. The reaction of OH radicals with DMM occurs via an H-atom abstraction mechanism with 76% of the attack occurring on the $-CH_3$ end groups and 24% on the central $-CH_2-$ unit. The atmospheric fate of the alkoxy radicals $CH_3OCH_2OCH_2O(\bullet)$ and $CH_3OCHO(\bullet)OCH_3$ at 296 K in 700 Torr of air was investigated using an FTIR-smog chamber technique. The sole atmospheric fate of $CH_3OCHO(\bullet)OCH_3$ radicals is reaction with O_2 to give dimethyl carbonate ($CH_3OC(O)OCH_3$) and HO_2 radicals. At least three loss processes were identified for $CH_3OCH_2OCH_2O(\bullet)$ radicals. In 1 atm of air at 295 K, 84 ± 4% of the $CH_3OCH_2OCH_2O(\bullet)$ radicals react with O_2 while 7 ± 3% undergo H-atom elimination; the fate of the remaining 9% is unclear. OH radical-initiated oxidation of DMM in 1 atm of air at 296 K results in a yield of 24% dimethyl carbonate and 69% methoxymethyl formate; the oxidation mechanism of the remaining 7% of DMM is unclear. Relative rate techniques were used to measure rate constants for the reaction of Cl atoms with $CH_3OCH_2OCH_3$ and CH_3OCH_2OCHO of $(1.4 \pm 0.2) \times 10^{-10}$ and $(3.6 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. Results are discussed in the context of the atmospheric chemistry of DMM.

1. Introduction

There are commercial and environmental pressures on vehicle manufacturers to produce vehicles with increased fuel economy. Diesel engines operate at a greater compression ratio and have a greater thermodynamic efficiency than gasoline engines. Increased use of diesel engines is an attractive method to increase fuel economy. Unfortunately, diesel engines running on conventional fuels have a tendency to produce substantial particulate emissions. Dimethyl ether (DME) has been proposed as a possible alternative diesel fuel because it combines acceptable fuel properties (i.e., high cetane number) with low exhaust emissions (especially particulate) and low combustion noise.[1,2] Dimethoxymethane (also known as methylal and formaldehyde dimethyl acetal) is a widely used solvent and possesses a molecular structure that is similar to dimethyl ether and has been proposed as a new diesel fuel. Under ambient conditions DME is a gas (bp, −25 °C), while dimethoxymethane (DMM) is a liquid (bp, 41 °C). Hence, DMM is easier to handle than DME. The atmospheric chemistry of automotive fuels and fuel additives is a subject of significant practical interest. The atmospheric oxidation of DME has been studied in our laboratories.[3−7] We report here the results of a study of the atmospheric chemistry of DMM.

Atmospheric degradation of DMM is initiated by OH radical attack, which proceeds via H-atom abstraction to give two different alkyl radicals:

$$CH_3OCH_2OCH_3 + OH \rightarrow CH_3OCH_2OCH_2(\bullet) + H_2O \quad (1a)$$

$$CH_3OCH_2OCH_3 + OH \rightarrow CH_3OCH(\bullet)OCH_3 + H_2O \quad (1b)$$

Under atmospheric conditions, the alkyl radicals produced in reaction 1 will rapidly (within 1 μs) add oxygen to give the corresponding peroxy radicals:

$$CH_3OCH_2OCH_2(\bullet) + O_2 + M \rightarrow CH_3OCH_2OCH_2O_2(\bullet) + M \quad (2a)$$

$$CH_3OCH(\bullet)OCH_3 + O_2 + M \rightarrow CH_3OCHO_2(\bullet)OCH_3 + M \quad (2b)$$

Peroxy radicals react with NO, NO_2, HO_2, and other peroxy radicals ($R'O_2$). Reaction with NO dominates in polluted air masses and is expected to give largely, if not exclusively, the corresponding alkoxy radical. In the present work, we have determined the rate constant of reaction 1, the atmospheric fate of the alkoxy radicals, $CH_3OCH_2OCH_2O(\bullet)$ and $CH_3OCHO(\bullet)OCH_3$, and the rate constants for the reaction of Cl atoms with dimethoxymethane and methoxymethyl formate.

2. Experimental Section

The experimental systems used have been described previously[8,9] and are only discussed briefly here.

2.1. Pulse Radiolysis Setup. A pulse radiolysis transient UV absorption apparatus was used to study the kinetics of the reaction of OH radicals with $CH_3OCH_2OCH_3$. OH radicals

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were generated by radiolysis of gas mixtures of $CH_3OCH_2OCH_3$ and H_2O in either argon or SF_6 diluent at 346 ± 3 K in a 1 L stainless steel reactor. A 30 ns pulse of 2 MeV electrons from a Febetron 705B field emission accelerator was used to initiate the reactions. The yield of OH radicals using argon as a bath gas was approximately 5×10^{14} cm^{-3}.

The analyzing light was obtained from a pulsed xenon arc lamp and reflected in the reaction cell by internal White type optics. The optical path length used in this work was 80 cm. The analyzing light was monitored by a 1 m McPherson monochromator linked to a Hamamatsu R928 photomultiplier and a LeCroy 9450A oscilloscope. The monochromator was operated at a spectral resolution of either 0.08 nm when detecting OH radicals at 309.1 nm, or 0.8 nm when detecting the radicals formed from reaction 1 at 280 nm. The temperature was measured using a platinum thermometer in the center of the reaction cell.

Reagents used were the following: $CH_3OCH_2OCH_3$ (>99%), 1−10 mbar, supplied by Aldrich; H_2O (three times distilled), 70−130 mbar; Ar (>99.998%), 860−930 mbar, delivered by Hede Nielsen; SF_6 (>99.9%), 900 mbar, supplied by Gerling and Holz. Reagents were used as received.

2.2. FTIR-Smog Chamber Setup. The FTIR system was interfaced to a 140 L Pyrex reactor. Radicals were generated by the UV irradiation of mixtures of 8−16 mTorr of $CH_3OCH_2OCH_3$, 34−300 mTorr of Cl_2 or 100−110 mTorr of CH_3ONO, and 5−700 Torr of O_2 in 700 Torr total pressure with N_2 diluent at 296 K using 22 black-lamps (760 Torr = 1013 mbar). The loss of reactants and the formation of products were monitored by FTIR spectroscopy, using an analyzing path length of 27 m and a resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added spectra. Reactants and products were monitored using their characteristic features over the entire wavenumber range. Reference spectra were acquired and calibrated by expanding known volumes of reference materials into the reactor. Methoxymethyl formate was synthesized by heating a 3-fold molar excess of sodium formate with chloromethyl methyl ether at 50 °C.[10] The ester was purified by simple distillation (bp, 102 °C/750 mmHg; lit., 103.6 °C/762 mmHg).[11] Gas chromatography−mass spectroscopy showed only one compound whose fragmentation pattern was consistent with methoxymethyl formate.

3. Results

3.1. Absolute Rate Measurement of $k(OH + CH_3OCH_2OCH_3)$. OH radicals were generated by pulse radiolysis of mixtures of 70−130 mbar of H_2O, 1−10 mbar of $CH_3OCH_2OCH_3$, and 860−930 mbar of Ar at 346 ± 3 K:

$$\mathrm{Ar} + 2\ \mathrm{MeV}\ e^- \rightarrow \mathrm{Ar}^* \qquad (3)$$

$$\mathrm{Ar}^* + H_2O \rightarrow OH + \mathrm{products} \qquad (4)$$

$$\mathrm{Ar}^* + CH_3OCH_2OCH_3 \rightarrow \mathrm{products} \qquad (5)$$

Ar* denotes metastable Ar atoms. To minimize interaction of Ar* with $CH_3OCH_2OCH_3$, reaction 5, H_2O concentrations were always at least 10 times that of $CH_3OCH_2OCH_3$. To obtain such concentration ratios, it was necessary to conduct the pulse radiolysis experiments at elevated temperature; 346 K was chosen as a convenient temperature at which to work.

In our first attempt to measure k_1 we monitored the decay rate of OH radicals via their absorption at 309.1 nm. This technique has been used extensively in our laboratory to measure the reaction rate of OH with a variety of compounds.[12−14] Unfortunately, the alkyl radicals formed in the reaction of OH radicals with $CH_3OCH_2OCH_3$ also absorb at 309.1 nm. This was verified by radiolysis of a mixture of $CH_3OCH_2OCH_3$ and SF_6. Radiolysis of SF_6 gives F atoms,[15] which abstract a hydrogen atom from $CH_3OCH_2OCH_3$. The absorption cross section of the primary radicals formed from the reaction of F atoms with $CH_3OCH_2OCH_3$ at 309.1 nm was comparable to the absorption of OH radicals, making it impossible to derive k_1 from the absorption at this wavelength.

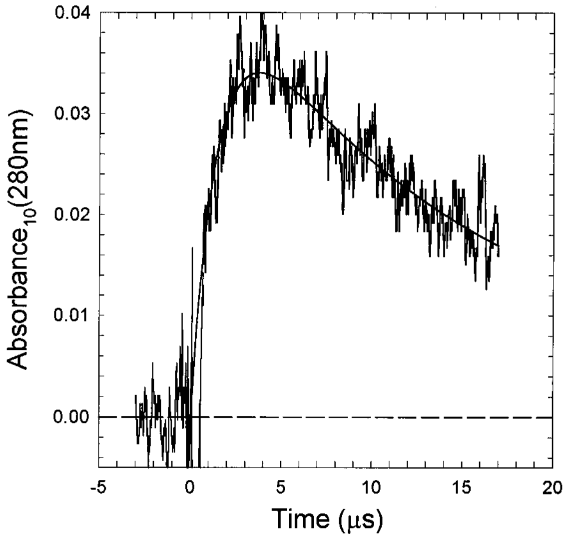

Figure 1. Transient absorption at 280 nm observed following radiolysis of a mixture of 6.04 mbar $CH_3OCH_2OCH_3$, 90 mbar H_2O, and 904 mbar of Ar. The smooth curve is a fit to expression I, which gives $k_{form} = (7.0 \pm 0.5) \times 10^5$ s^{-1}.

To measure k_1, a monitoring wavelength other than 309.1 nm has to be used. Following radiolysis of a mixture of 6.04 mbar of $CH_3OCH_2OCH_3$, 90 mbar of H_2O, and 904 mbar of Ar, the transient absorption at 280 nm shown in Figure 1 was observed. The rate of formation of this absorbance increased with increasing amounts of $CH_3OCH_2OCH_3$. OH radicals do not absorb appreciably at 280 nm, and it seems reasonable to attribute the absorbance at 280 nm observed following pulsed radiolysis of $CH_3OCH_2OCH_3/H_2O/Ar$ mixtures to one or both of the alkyl radicals formed in reaction 1.

As seen from Figure 1, the formation of radicals from reaction 1 absorbing at 280 nm was followed by a decay. To determine the rate constant for reaction 1, experimental transients were fitted by the following expression using k_{form}, k_{decay}, and A_{max} as parameters:

$$A(t) = \frac{k_{form} A_{max}}{k_{form} - k_{decay}} [\exp(-k_{decay}t) - \exp(-k_{form}t)] \qquad (I)$$

k_{form} and k_{decay} are the pseudo-first-order formation and loss rates, respectively, $A(t)$ is the absorbance as function of time, and A_{max} is the maximum transient absorbance if $k_{decay} = 0$. This expression is an approximation because although both alkyl radicals are formed with the same pseudo-first-order rate constant, they may have different decay kinetics (also their decays may not be strictly first order). Expression I assumes that OH loss processes other than reaction 1 are first order in OH and neglects the possible importance of secondary reactions of OH radicals with the alkyl radicals formed in reaction 1. Nevertheless, it was found that expression I always gave good fits to the experimental absorption transients; an example is shown in Figure 1. In Figure 2, k_{form} is plotted as a function of the initial pressure of $CH_3OCH_2OCH_3$. The line is a linear least-squares fit giving $k_1 = (4.6 \pm 0.7) \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}. The intercept in Figure 2 is $(9 \pm 5) \times 10^4$ s^{-1} and can be

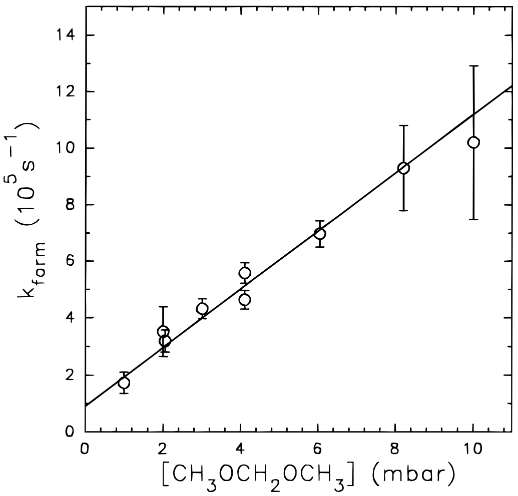

Figure 2. Plot of k_{form} versus the dimethoxymethane concentration.

attributed to loss of OH radicals via self-reaction and reaction with the alkyl radicals formed in reaction 1. Errors quoted thus far are statistical. The intercept in Figure 2 suggests that an additional ~10% uncertainty arises from non-pseudo-first order behavior. Finally, we estimate that there is a 10% systematic uncertainty in k_1 associated with pressure calibrations and reagent impurities. Hence, we report $k_1 = (4.6 \pm 1.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

3.2. Relative Rate Measurement of k(OH + $CH_3OCH_2OCH_3$). The kinetics of reaction 1 were studied using a relative rate technique at Ford Motor Company as described elsewhere.[16] Mixtures of 16 mTorr of DMM, 100−110 mTorr of CH_3ONO, and either 20 mTorr of C_2H_4 or 8−16 mTorr of cyclohexane in 700 Torr of air were subjected to UV irradiation in the FTIR-smog chamber system at Ford Motor Company. OH radicals are produced by reactions 6−8 and then react either with DMM or with the reference compound (C_2H_4 or cyclohexane):

$$CH_3ONO + h\nu \rightarrow CH_3O + NO \tag{6}$$

$$CH_3O + O_2 \rightarrow HO_2 + HCHO \tag{7}$$

$$HO_2 + NO \rightarrow OH + NO_2 \tag{8}$$

$$CH_3OCH_2OCH_3 + OH \rightarrow \text{products} \tag{1}$$

$$OH + C_2H_4 \rightarrow \text{products} \tag{9}$$

$$OH + c\text{-}C_6H_{12} \rightarrow \text{products} \tag{10}$$

The kinetics of reactions 9 and 10 are well established. In 700 Torr of air diluent at 296 K, $k_9 = 8.52 \times 10^{-12}$ and $k_{10} = 7.49 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[17] Figure 3 shows plots of the loss of DMM versus those of C_2H_4 and cyclohexane. Linear least-squares analysis gives $k_1/k_9 = 0.59 \pm 0.05$ and $k_1/k_{10} = 0.74 \pm 0.08$. Hence, values of $k_1 = (5.0 \pm 0.4) \times 10^{-12}$ and $(5.5 \pm 0.6) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} are derived. Consistent results were obtained using the two different reference compounds. We choose to quote the average of the results above with error limits that encompass the extremes of the ranges; hence, $k_1 = (5.3 \pm 0.8) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. We estimate that potential systematic errors associated with uncertainties in the reference rate constants could add an additional 10% to the uncertainty range. Propagating this additional 10% uncertainty gives $k_1 = (5.3 \pm 1.0) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. This result is, within the experimental uncertainties, indistinguishable from that found using the pulse radiolysis technique in section 3.1 at 346 K and also from values of $k_1 = (4.9 \pm 0.8) \times 10^{-12}$ and $(4.6 \pm 0.1) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K reported by Porter et al.[18]

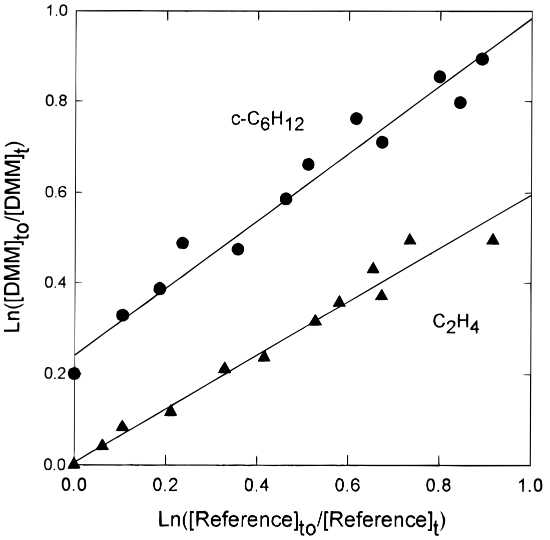

Figure 3. Plots of the loss of dimethoxymethane versus those of c-C_6H_{12} and C_2H_4 when mixtures containing these compounds were exposed to OH radicals in 700 Torr of air at 296 K. Data using c-C_6H_{12} reference have been shifted upward by 0.2 units for clarity.

3.3. Kinetics of the Reactions of Cl Atoms with $CH_3OCH_2OCH_3$ and CH_3OCH_2OCHO. Prior to the investigation of the atmospheric fate of $CH_3OCH_2OCH_2O(\bullet)$ and $CH_3OCHO(\bullet)OCH_3$ radicals, a series of relative rate experiments were performed using the FTIR system to investigate the kinetics of the reactions of Cl atoms with $CH_3OCH_2OCH_3$ (DMM) and CH_3OCH_2OCHO (MMF). The techniques used are described in detail elsewhere.[19] Photolysis of molecular chlorine was used as a source of Cl atoms:

$$Cl_2 + h\nu \rightarrow 2Cl \tag{11}$$

$$Cl + CH_3OCH_2OCH_3\ (\text{DMM}) \rightarrow \text{products} \tag{12}$$

$$Cl + CH_3OCH_2OCHO\ (\text{MMF}) \rightarrow \text{products} \tag{13}$$

The kinetics of reaction 12 were measured relative to reactions 14 and 15, and reaction 13 was studied relative to reactions 14 and 16.

$$Cl + C_2H_4 \rightarrow \text{products} \tag{14}$$

$$Cl + n\text{-}C_4H_{10} \rightarrow \text{products} \tag{15}$$

$$Cl + CH_3OH \rightarrow \text{products} \tag{16}$$

The observed loss of DMM and MMF versus that of the reference compounds following the UV irradiation of DMM/reference/Cl_2 and MMF/reference/Cl_2 mixtures in 700 Torr total pressure of N_2 or air diluent is shown in Figures 4 and 5. There was no discernible difference between data obtained in N_2 or air diluent. Linear least-squares analysis gives $k_{12}/k_{14} = 1.40 \pm 0.09$, $k_{12}/k_{15} = 0.67 \pm 0.04$, $k_{13}/k_{14} = 0.39 \pm 0.04$, and $k_{13}/k_{16} = 0.63 \pm 0.06$. Using $k_{14} = 9.4 \times 10^{-11}$,[20] $k_{15} = 2.05 \times 10^{-10}$,[21] and $k_{16} = 5.4 \times 10^{-11}$ [20] gives $k_{12} = (1.3 \pm 0.1) \times 10^{-10}$, $k_{12} = (1.4 \pm 0.1) \times 10^{-10}$, $k_{13} = (3.7 \pm 0.4) \times 10^{-11}$, and $k_{13} = (3.4 \pm 0.3) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, respectively. Consistent results were obtained using the different reference compounds. We choose to quote values for k_{12} and k_{13}, which

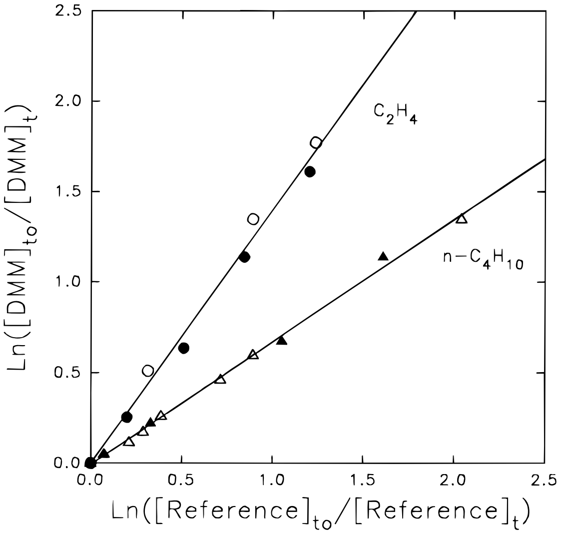

Figure 4. Plots of the loss of dimethoxymethane versus those of C_2H_4 (circles) and n-C_4H_{10} (triangles) when mixtures containing these compounds were exposed to Cl atoms in 700 Torr of air (filled symbols) or N_2 (open symbols) at 296 K.

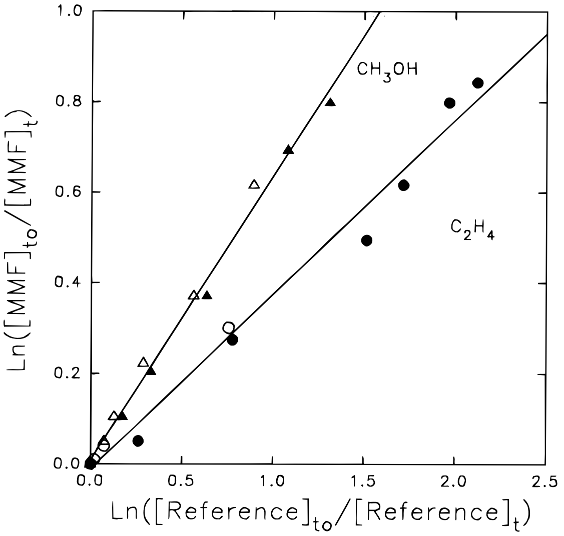

Figure 5. Plots of the loss of methoxymethyl formate versus those of C_2H_4 (circles) and CH_3OH (triangles) when mixtures containing these compounds were exposed to Cl atoms in 700 Torr of O_2 (filled symbols) or N_2 (open symbols) at 296 K.

are averages of the results above with error limits that encompass the extremes of the ranges; hence, $k_{12} = (1.35 \pm 0.15) \times 10^{-10}$ and $k_{13} = (3.55 \pm 0.45) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. We estimate that potential systematic errors associated with uncertainties in the reference rate constants could add an additional 10% to the uncertainty range. Propagating this additional 10% uncertainty gives $k_{12} = (1.4 \pm 0.2) \times 10^{-10}$ and $k_{13} = (3.6 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. There are no literature data to compare with our results.

3.4. Atmospheric Fate of Alkoxy Radicals Derived from $CH_3OCH_2OCH_3$. When DMM is oxidized in the atmosphere, two different alkoxy radicals are formed depending on the site of OH reaction: $CH_3OCH_2OCH_2O(\bullet)$ and $CH_3OCHO(\bullet)OCH_3$. To determine the atmospheric fate of these alkoxy radicals, experiments were performed in which $Cl_2/CH_3OCH_2OCH_3/O_2/NO$ mixtures at a total pressure of 700 Torr (N_2 diluent) were irradiated in the FTIR-smog chamber system. Loss of DMM and formation of products were monitored by FTIR spectroscopy. By analogy to the behavior of other peroxy radicals,[22,23] it is expected that alkoxy radicals will be formed in the chamber by the reaction of peroxy radicals with NO:

$$CH_3OCH_2OCH_2O_2(\bullet) + NO \rightarrow CH_3OCH_2OCH_2O(\bullet) + NO_2 \quad (17a)$$

$$CH_3OCHO_2(\bullet)OCH_3 + NO \rightarrow CH_3OCHO(\bullet)OCH_3 + NO_2 \quad (17b)$$

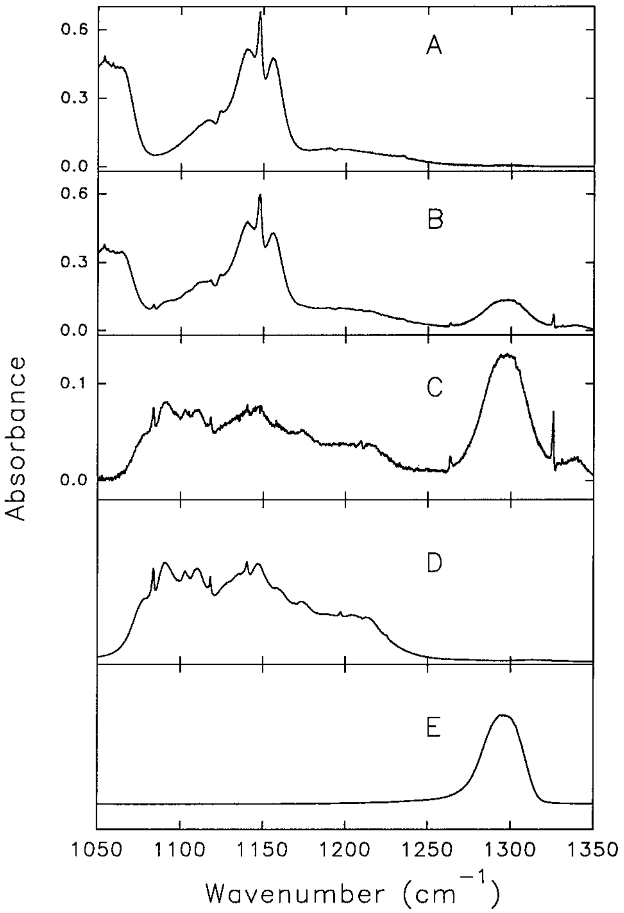

Figure 6. Infrared spectra acquired before (A) and after (B) a 15 s irradiation of a mixture of 15.4 mTorr of dimethoxymethane, 101 mTorr of Cl_2, 25.1 mTorr of NO, and 600 Torr of O_2 in 700 Torr total pressure with N_2 diluent. Panel C shows the result of stripping dimethoxymethane features from panel B. Panels D and E show reference spectra of methoxymethyl formate and dimethyl carbonate, respectively.

Figure 6 shows typical IR spectra acquired before and after a 15 s irradiation of a mixture of 15.4 mTorr of dimethoxymethane, 101 mTorr of Cl_2, 25.1 mTorr of NO, and 600 Torr of O_2 in 700 Torr total pressure with N_2 diluent. Subtraction of IR features attributable to dimethoxymethane from panel B gives panel C; the loss of dimethoxymethane was 3.39 mTorr. Comparison of panel C with reference spectra of methoxymethyl formate and dimethyl carbonate in panels D and E, respectively, shows the formation of 0.84 mTorr of methoxymethyl formate and 2.38 mTorr of dimethyl carbonate. The product features at 1263 and 1326 cm^{-1} are attributable to the formation of HONO and HNO_3 via reaction of OH radicals with NO and NO_2, respectively. In all experiments, methoxymethyl formate and dimethyl carbonate were observed as major products. For experiments employing O_2 partial pressures greater than 200 Torr the combined yields of methoxymethyl formate and dimethyl carbonate accounted for 95−98% of the loss of DMM. HCHO was observed as a minor product. The molar yield of HCHO increased as the O_2 partial pressure was decreased. In the presence of 6 Torr of O_2, the molar HCHO

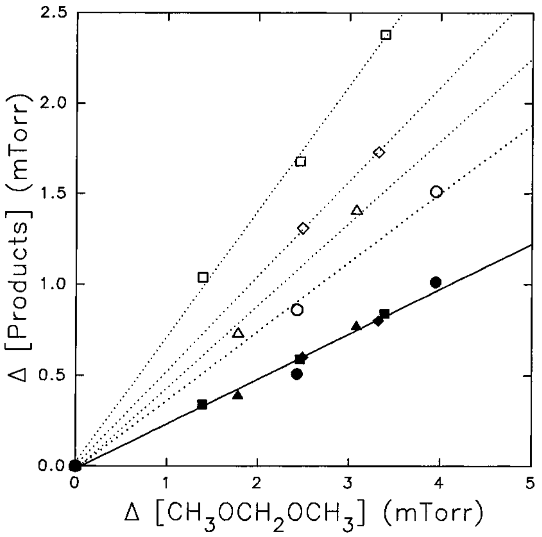

Figure 7. Formation of methoxymethyl formate (open symbols) and dimethyl carbonate (filled symbols) versus loss of dimethoxymethane following UV irradiation of DMM/Cl_2/NO/O_2/N_2 mixtures. All experiments were performed at 296 K and 700 Torr total pressure. The O_2 partial pressures used were 600 (squares), 29 (diamonds), 18 (triangles), and 6 (circles) Torr. The dotted lines are linear regressions through the methoxymethyl formate data sets. The solid line is a linear regression of the entire dimethyl carbonate data set.

yield was 64% . In addition, trace amounts of methyl formate (molar yield <5%) were observed in the presence of 6 Torr of O_2. The carbon balance decreased with decreasing O_2 partial pressure. In the presence of 6 Torr of O_2, the combined yield of the observed carbon containing products (methoxymethyl formate, dimethyl carbonate, formaldehyde, and methyl formate) accounted for 76% of the loss of DMM. After subtraction of IR features belonging to these products residual IR product features remained at 758, 824, and 1690 cm^{-1} because of one or more unidentified products.

Figure 7 shows plots of the formation of methoxymethyl formate and dimethyl carbonate versus the loss of DMM for experiments conducted at 700 Torr total pressure with either 8, 18, 29, or 600 Torr partial pressure of O_2 diluent. As with all product studies, careful attention needs to be given to the possible loss of products via secondary reactions. In the present experiments, secondary reactions with Cl atoms and OH radicals are possible. Reaction of Cl atoms with dimethoxymethane proceeds with a rate constant that is 4 times that with methoxymethyl formate and 61 ($1.4 \times 10^{-10}/2.3 \times 10^{-12}$[24]) times that with dimethyl carbonate. The rate constant for reaction of OH radicals with dimethoxymethane is 17 ($5.3 \times 10^{-12}/3.1 \times 10^{-13}$[24]) times that with dimethyl carbonate. The rate of reaction of OH radicals with MMF is unknown. The loss of dimethoxymethane used in the present work was 2−22%. For such conversions, loss of dimethyl carbonate via reactions with Cl and OH will be negligible. In the absence of data for the OH + MMF reaction, it is not possible to assess the magnitude of possible loss of this compound. In all experiments, product yield plots such as those shown in Figure 7 were, within the experimental uncertainties, linear. Thus, the experimental observations suggest that secondary loss of MMF is not significant.

As seen from Figures 7 and 8, the yield of dimethyl carbonate was independent of O_2 partial pressure. Linear least-squares analysis of data gives a molar yield of dimethyl carbonate of 25 ± 2%. The fact that the dimethyl carbonate yield is not impacted by changes in the O_2 partial pressure over the range 5.6−600 Torr shows that the atmospheric fate of the alkoxy radical $CH_3OCHO(\bullet)OCH_3$ is reaction with O_2, elimination of an H-atom, or both:

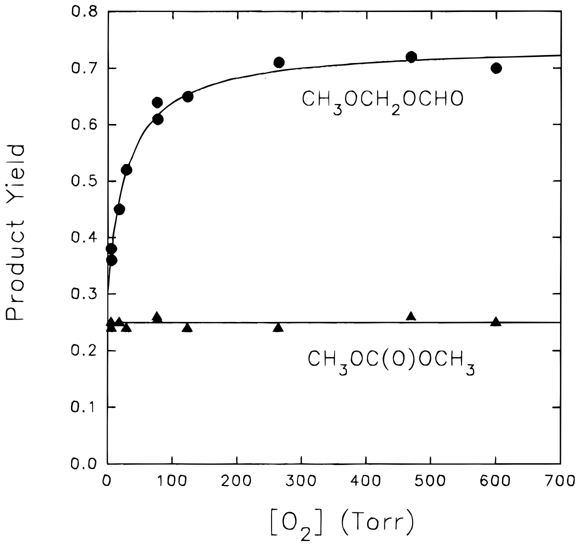

Figure 8. Observed yields of methoxymethyl formate (●) and dimethyl carbonate (▲) versus the O_2 partial pressure. The curve through the methoxymethyl formate data is a fit (see text for details). The line through the dimethyl carbonate data reflects a constant yield of 0.25.

$$CH_3OCHO(\bullet)OCH_3 + O_2 \rightarrow CH_3OC(O)OCH_3\ (DMC) + HO_2 \quad (18)$$

$$CH_3OCHO(\bullet)OCH_3 + M \rightarrow CH_3OC(O)OCH_3\ (DMC) + H + M \quad (19)$$

In contrast to the behavior of dimethyl carbonate, the yield of methoxymethyl formate was sensitive to the O_2 partial pressure. Figure 8 shows a plot of the molar yield of methoxymethyl formate versus [O_2] following irradiation of mixtures of 15−17 mTorr of DMM, 7−25 mTorr of Cl_2, 6−23 mTorr of NO, and 6−600 Torr of O_2 in 700 Torr total pressure with N_2 diluent. The fact that the yield of MMF drops when [O_2] is decreased below ~200 Torr shows that additional loss mechanisms become important for either the alkyl, alkyl peroxy, or alkoxy radical. It is conceivable that reaction with Cl_2 and/or NO competes with O_2 for the available alkyl and/or alkoxy radicals. To test for the effect of [O_2] and [Cl_2] on the observed product yields, experiments were performed with [O_2] = 6 Torr and [NO] and [Cl_2] varied independently over the ranges 6−23 and 7−50 mTorr, respectively. There was no observable effect of [Cl_2] over the range stated. For experiments in which [NO] was varied, there was no difference between experiments using [NO] = 6 or 12 mTorr; but with [NO] = 25 mTorr, the yields of MMF and DMC decreased slightly. With [NO] = 25 mTorr, the yields of MMF and DMC were 31 ± 2% and 21 ± 2%, respectively, while with [NO] = 6 or 12 mTorr the yields were 37 ± 2% and 25 ± 2%. This observation presumably reflects competition of NO with O_2 for the alkoxy radicals at low [O_2]. Accordingly, for experiments with [O_2] < 100 Torr, only data from experiments with [NO] < 13 mTorr were used to derive the data shown in Figure 8.

As seen from Figure 8, the yield of methoxymethyl formate, although sensitive to the O_2 partial pressure, does not approach zero at the lowest O_2 pressures studied. Such behavior suggests that there are two pathways by which methoxymethyl formate is formed in the chamber; one pathway is dependent upon O_2, the other is not. The trend of the data shown in Figure 8 suggests that there are at least three competing fates for the $CH_3OCH_2OCH_2O(\bullet)$ radicals:

$$CH_3OCH_2OCH_2O(\bullet) + O_2 \rightarrow CH_3OCH_2OCHO\ (MMF) + HO_2 \quad (20)$$

$$CH_3OCH_2OCH_2O(\bullet) + M \rightarrow CH_3OCH_2OCHO\ (MMF) + H + M \quad (21)$$

$$CH_3OCH_2OCH_2O(\bullet) \rightarrow \text{other products} \quad (22)$$

The expected dependence of the yield of MMF on the O_2 partial pressure can be expressed as

$$Y(CH_3OCH_2OCH_2O) = Y(CH_3OCH_2OCH_2O(\bullet))\left(\frac{\left(\frac{k_{20}}{k_{21}}\right)[O_2] + 1}{\left(\frac{k_{20}}{k_{21}}\right)[O_2] + 1 + \left(\frac{k_{22}}{k_{21}}\right)}\right)$$

where $Y(CH_3OCH_2OCH_2O(\bullet))$ is the molar yield of $CH_3OCH_2OCH_2O(\bullet)$ radicals in the system. The above expression was fitted to the data in Figure 8 with three parameters varied simultaneously: k_{20}/k_{21}, k_{22}/k_{21}, and $Y(CH_3OCH_2OCH_2O(\bullet))$. Best fit values of $k_{20}/k_{21} = 0.08 \pm 0.04$ Torr^{-1}, $k_{22}/k_{21} = 1.5 \pm 0.3$, and $Y(CH_3OCH_2OCH_2O(\bullet)) = 0.74 \pm 0.05$ were obtained. As discussed above, $CH_3OCHO(\bullet)OCH_3$ radicals react to give dimethyl carbonate. Hence, $Y(CH_3OCH_2OCH_2O(\bullet)) = 1 - Y(DMC)$. The DMC yield in all experiments was 25 ± 2%, so the expected value of $Y(CH_3OCH_2OCH_2O(\bullet))$ is 0.75 ± 0.02, which is in good agreement with the value of 0.74 ± 0.05 derived from the fit to the data in Figure 8. By use of the values of k_{20}/k_{21} and k_{22}/k_{21} derived above, it can be calculated that in the presence of 1 atm of air diluent ($[O_2] = 160$ Torr), reactions 20−22 account for 84 ± 4%, 7 ± 3%, and 9 ± 5% of the fate of $CH_3OCH_2OCH_2O(\bullet)$ radicals, respectively.

Thus far, we have not addressed the products of reaction 22. In addition to reactions 20 and 21, possible fates of $CH_3OCH_2OCH_2O(\bullet)$ radicals include decomposition and isomerization via internal H-atom abstraction. Eberhard et al.[25] and Atkinson and Aschmann[26] have shown that isomerization is important for aliphatic C_6 and C_7 alkoxy radicals. The analysis presented above is unaffected by the exact mechanism of the reaction 22. For experiments conducted with low O_2 partial pressures, HCHO and methyl formate were observed as minor products. The relative yield of [HCHO]/[methyl formate] ≈ 10 provides some insight into reaction 22. The most likely decomposition route for the $CH_3OCH_2OCH_2O(\bullet)$ radicals would give HCHO and the alkoxy radical $CH_3OCH_2O(\bullet)$. Under the present experimental conditions, any $CH_3OCH_2O(\bullet)$ formed is expected to be converted into methyl formate. The fact that the observed [HCHO]/[methyl formate] ratio was ∼10 suggests that decomposition via reaction 23 is of minor importance.

$$CH_3OCH_2OCH_2O(\bullet) \rightarrow CH_3OCH_2O\,(\bullet) + HCHO \quad (23)$$

The isomerization reaction 24 may lead to the formation of three molecules of HCHO:

$$CH_3OCH_2OCH_2O(\bullet) \rightarrow (\bullet)CH_2OCH_2OCH_2OH \quad (24)$$

$$(\bullet)CH_2OCH_2OCH_2OH \rightarrow HCHO + HCHO + (\bullet)CH_2OH \quad (25)$$

$$(\bullet)CH_2OH + O_2 \rightarrow HCHO + HO_2 \quad (26)$$

The observed [HCHO]/[methyl formate] yield ratio of ∼10 suggests that isomerization is more important than C−O bond scission.

Finally, we need to consider how our results fit in with the available data concerning the atmospheric degradation mechanisms of other alkoxy radicals. The results from the present work show that under atmospheric conditions at least three loss mechanisms compete for $CH_3OCH_2OCH_2O(\bullet)$ radicals. A similar conclusion was reached in a recent study of the alkoxy radical derived from dimethyl carbonate, $CH_3OC(O)OCH_2O(\bullet)$.[24] There are obvious structural similarities between this alkoxy radical and that derived from dimethyl carbonate, so similar behavior is reasonable.

Veyret et al. and Jenkin et al. have presented evidence for H atom elimination from $HOCH_2O$ and CH_3OCH_2O radicals, with rates at 298 K of $k_{36} \approx 1200$ s^{-1} [27] and $k_{37} \approx 3000$ s^{-1}:[3]

$$HOCH_2O + M \rightarrow HCOOH + H + M \quad (27)$$

$$CH_3OCH_2O + M \rightarrow CH_3OCHO + H + M \quad (28)$$

From $k_{20}/k_{21} = 0.08$ Torr^{-1} and assuming $k_{20} \approx 10^{-14}$ cm^3 molecule^{-1} s^{-1} (typical for such a reaction), an estimate of $k_{21} = 4 \times 10^3$ s^{-1} is obtained that is broadly comparable to the rates of the analogous reactions 27 and 28. It appears that H atom elimination may be a general decomposition mechanism for alkoxy radicals bearing an oxygen functionality.

Finally, we can compare our results with those obtained by Porter et al.[28] from a study of the Cl atom-initiated oxidation of DMM in the absence of NO_x. Consistent with the present study, Porter et al. observed the formation of methyl formate, dimethyl carbonate, and methoxymethyl formate products. However, in contrast to the present study, the relative product yields in the study by Porter et al. were not effected by variation of the O_2 partial pressure over the range 1−760 Torr. It does not seem likely that the different behavior observed by Porter et al. can be attributed to the absence of NO_x in their study. The origin of the discrepancy is unknown.

3.5. Mechanism of the Reaction of OH Radicals with $CH_3OCH_2OCH_3$. To establish the relative importance of reactions 1a and 1b, mixtures of 15−17 mTorr of dimethoxymethane, 54−104 mTorr of CH_3ONO, and 8−11 mTorr of NO were subjected to UV irradiation in the FTIR-smog chamber system:

$$CH_3OCH_2OCH_3 + OH \rightarrow CH_3OCH_2OCH_2(\bullet) + H_2O \quad (1a)$$

$$CH_3OCH_2OCH_3 + OH \rightarrow CH_3OCH(\bullet)OCH_3 + H_2O \quad (1b)$$

Figure 9 shows a plot of the observed formation of dimethyl carbonate yield versus the loss of dimethoxymethane. Linear least-squares analysis gives a dimethyl carbonate yield of 24 ± 2%. As shown in section 3.4, dimethyl carbonate provides a marker for the formation of $CH_3OCH(\bullet)OCH_3$ radicals. Hence, we conclude that $k_{1b}/(k_{1a} + k_{1b}) = 0.24 \pm 0.02$, and by inference, $k_{1a}/(k_{1a} + k_{1b}) = 0.76 \pm 0.02$. The relative importance of H atom abstraction from the two possible sites in dimethoxymethane is directly proportional to the number of different C−H bonds.

4. Discussion

A substantial body of kinetic and mechanistic data pertaining to the atmospheric chemistry of dimethoxymethane is presented here. It is expected that the atmospheric lifetime of DMM is determined by reaction with OH radicals. Although the OH

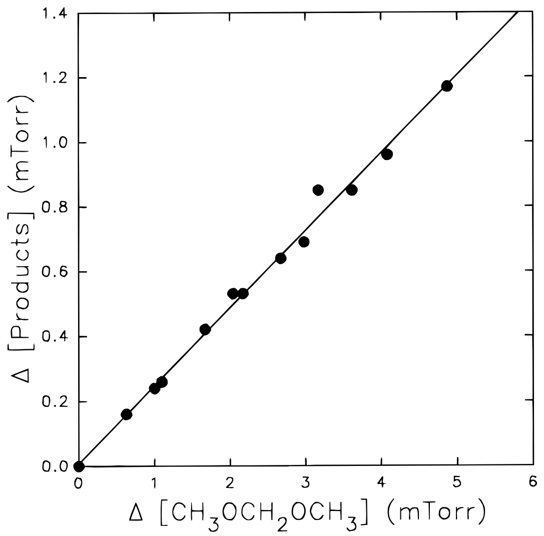

Figure 9. Formation of dimethyl carbonate versus loss of dimethoxymethane observed following UV irradiation of DMM/CH_3ONO/NO mixtures in 700 Torr of air diluent.

radical concentration in the atmosphere varies with location, time of day, season, and meteorological conditions, a reasonable 24 h global average is (0.5−1.0) × 10^6 cm^{-3}.[29−31] At 296 K, the rate constant for reaction of OH radicals with dimethoxymethane is 5.3 × 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Hence, the atmospheric lifetime of dimethoxymethane is 2−4 days. Attack of OH radicals proceeds at the $-CH_2-$ group 24% of the time to give an alkyl radical that, in the presence of NO_x, gives dimethyl carbonate exclusively. Attack of OH radicals proceeds at the $-CH_3$ groups 76% of the time. The resulting alkoxy radical is converted into methoxymethyl formate with an efficiency of 91%, i.e., we expect a methoxymethyl formate yield of 0.91 × 0.76 = 69% . The mechanism of the oxidation of the remaining 7% of DMM is unclear.

From the viewpoint of understanding the atmospheric degradation mechanism of organic compounds, it is interesting to note that the alkoxy radical derived from DMM undergoes three competing atmospheric loss processes. This is a very unusual case, since typically only one or two processes are important. Evidence is presented showing rapid H-atom elimination from the alkoxy radical derived from DMM. This seems to be a general decomposition mechanism for alkoxy radicals bearing an oxygen functionality.

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