

# Dimethyl Ether Oxidation: Kinetics and Mechanism of the $\text{CH}_3\text{OCH}_2 + \text{O}_2$ Reaction at 296 K and 0.38–940 Torr Total Pressure

J. Sehested\* and T. Møgelberg

Section for Chemical Reactivity, Environmental Science and Technology Department,  
Risø National Laboratory, DK-4000 Roskilde, Denmark

T. J. Wallington\* and E. W. Kaiser

Ford Motor Company, Mail Drop, SRL-3083, P.O. Box 2053, Dearborn, Michigan 48121-2053

O. J. Nielsen\*

Ford Motor Company, Ford Forschungszentrum Aachen, Dennewartsstrasse 25, D-52068 Aachen, Germany

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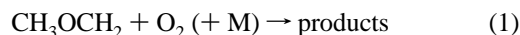
The title reaction was studied at 296 K and 0.38–940 Torr total pressure using a FTIR smog chamber technique. The overall rate constant for reaction of  $\text{CH}_3\text{OCH}_2$  radicals with  $\text{O}_2$  may be written,  $k_1 = k_{\text{RO}_2} + k_{\text{prod}}$ , where  $k_{\text{RO}_2}$  is the rate constant for peroxy radical production and  $k_{\text{prod}}$  is the rate constant for the production of other species from reaction 1.  $k_1$  was measured relative to the pressure independent reaction of  $\text{CH}_3\text{OCH}_2$  radicals with  $\text{Cl}_2$  ( $k_4$ ). There was no discernible effect of pressure on  $k_1$  in the range 200–940 Torr. Between 200 and 2 Torr total pressure  $k_1$  decreased by approximately a factor of 2. For pressures below 2 Torr  $k_1$  was again independent of pressure. The reaction proceeds via the formation of an activated complex,  $\text{CH}_3\text{OCH}_2\text{O}_2^\ddagger$ , that is either collisionally stabilized to form the peroxy radical,  $\text{CH}_3\text{OCH}_2\text{O}_2$ , or undergoes intramolecular H-atom abstraction followed by decomposition to give two formaldehyde molecules and an OH radical:  $\text{CH}_3\text{OCH}_2 + \text{O}_2 \rightleftharpoons \text{CH}_3\text{OCH}_2\text{O}_2^\ddagger$ ,  $\text{CH}_3\text{OCH}_2\text{O}_2^\ddagger + \text{M} \rightarrow \text{CH}_3\text{OCH}_2\text{O}_2 + \text{M}$ ,  $\text{CH}_3\text{OCH}_2\text{O}_2^\ddagger \rightarrow \text{CH}_2\text{OCH}_2\text{O}_2\text{H}^\ddagger \rightarrow 2\text{HCHO} + \text{OH}$ . The products from this reaction were studied as a function of total pressure. The molar yield of formaldehyde increased from <2% at 700 Torr total pressure to ~200% at 0.38 Torr total pressure, while the combined yield of methyl formate and methoxy methylhydroperoxide decreased from ~100% to 4% over the same pressure range. Fitting the product yields and relative rate data using a modified Lindemann expression gave the following rate constants:  $k_{\text{RO}_2,0}/k_4 = (1.97 \pm 0.28) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$ ,  $k_{\text{RO}_2,\infty}/k_4 = 0.108 \pm 0.004$ , and  $k_{\text{prod},0}/k_4 = (6.3 \pm 0.5) \times 10^{-2}$  where  $k_{\text{RO}_2,0}$  and  $k_{\text{RO}_2,\infty}$  are the overall termolecular and bimolecular rate constants for formation of the  $\text{CH}_3\text{OCH}_2\text{O}_2$  radical and  $k_{\text{prod},0}$  represents the bimolecular rate constant for the reaction of  $\text{CH}_3\text{OCH}_2$  radicals with  $\text{O}_2$  to yield formaldehyde in the limit of low pressure. These data and absolute rate data from the literature were used to derive a rate constant for the reaction of  $\text{CH}_3\text{OCH}_2$  radicals with  $\text{Cl}_2$  of  $(1.00 \pm 0.16) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The results are discussed in the context of the use of dimethyl ether as an alternative diesel fuel.

## 1. Introduction

Dimethyl ether (DME) has been proposed as an alternative diesel fuel by Topsøe and AMOCO.<sup>1</sup> Dimethyl ether has the following desirable properties that make it an attractive diesel fuel. First, it has a high cetane (i.e., low octane) number. Second, when used in diesel engines, it reduces combustion noise and emissions of particles. Third, the trade-off between  $\text{NO}_x$  emissions and soot using conventional diesel fuel is eliminated in DME-fueled engines because the combustion is soot-free. Hence, a DME-fueled engine can be tuned to give reduced  $\text{NO}_x$  emissions.<sup>1</sup> Fourth, DME can be produced from hydrocarbons via a relatively cheap one-step synthesis. Engine tests have shown that DME-fueled diesel engines have emission levels that surpass the California ultralow emissions vehicle (ULEV) regulation for medium duty vehicles.<sup>2</sup> Interestingly, ethers like MTBE (methyl *tert*-butyl ether), ETBE (ethyl *tert*-butyl ether), and TAME (*tert*-amyl methyl ether) have high

octane (i.e., low cetane) numbers and are used to boost the octane number of gasoline. It is surprising that DME, which is structurally similar to MTBE, ETBE, and TAME, has a high cetane number and hence is a good diesel fuel, while the other ethers have low cetane numbers and would make poor diesel fuels. A possible explanation for this difference is discussed below.

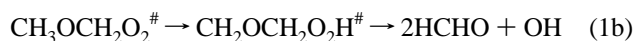
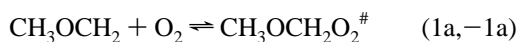
At this point it is germane to note that unlike conventional diesel fuel, DME is a gas at ambient temperature. Hence, any widespread use of DME would require significant investment in new infrastructure associated with fuel distribution and delivery. The atmospheric chemistry of DME has been studied by Japar et al.,<sup>3</sup> Jenkin et al.,<sup>4</sup> Wallington et al.,<sup>5</sup> and Langer et al.<sup>6</sup> Surprisingly high formaldehyde yields following Cl atom initiated oxidation of dimethyl ether in  $\text{N}_2/\text{O}_2$  diluent at total pressures below 300 Torr were reported by Jenkin et al.<sup>4</sup> It was suggested that formaldehyde was formed in the reaction of  $\text{CH}_3\text{OCH}_2$  radicals with  $\text{O}_2$ ,



\* To whom correspondence may be addressed.

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via the following mechanism:<sup>4</sup>



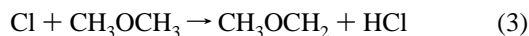
where formaldehyde is formed by intramolecular hydrogen transfer in the energetically excited  $\text{CH}_3\text{OCH}_2\text{O}_2^\#$  radical followed by decomposition, (reaction 1b). At sufficiently low pressures  $\text{CH}_3\text{OCH}_2\text{O}_2^\#$  radicals are not stabilized and reaction 1 proceeds essentially exclusively via reaction 1b. At higher pressures the highly energetic  $\text{CH}_3\text{OCH}_2\text{O}_2^\#$  complex is stabilized by collisional quenching to give thermalized  $\text{CH}_3\text{OCH}_2\text{O}_2$  radicals.  $\text{CH}_3\text{OCH}_2\text{O}_2$  radicals react to give  $\text{CH}_3\text{OCHO}$  and  $\text{CH}_3\text{OCH}_2\text{OOH}$  under atmospheric conditions.<sup>4</sup>

Alkylperoxy radicals are thermally unstable at > 1000 K and consequently are not important in high-temperature combustion chemistry. However, at lower temperature (500–950 K) alkylperoxy radicals have sufficient stability to assume an important role in autoignition phenomena, which cause unwanted audible mechanical vibrations in gasoline-fueled engines known as “knock”.<sup>7,8</sup> Isomerization reactions similar to reaction 1b are important sources of reactive free radicals that promote autoignition.<sup>9</sup> The importance of reaction 1b in the high-temperature oxidation of DME has been considered by Dagaut et al.<sup>10</sup> using a detailed kinetic modeling approach at temperatures of 850–1300 K and pressures of 1–10 bar. It was found that reaction 1b was an important loss of  $\text{CH}_3\text{OCH}_2$  radicals in their model at high pressures and low temperatures.<sup>10</sup> In terms of the use of DME as a diesel fuel, reaction 1b is desirable, since it propagates the reaction chain producing reactive OH radicals and formaldehyde. Combustion of formaldehyde gives little or no particulate matter.<sup>11</sup>

The objective of this work is to investigate the kinetics and mechanism of reaction 1. The results are discussed in the context of DME as an alternative diesel fuel.

## 2. Experimental Section

The apparatus and experimental technique used in this work have been described in detail previously<sup>12</sup> and are only briefly discussed here. Experiments were performed in a 140 L Pyrex reactor surrounded by 22 fluorescent blacklamps (GE F15T8-BL) that emit in the region 300–450 nm. Methoxy methyl radicals were generated by the photolysis of molecular chlorine in the presence of dimethyl ether with and without NO in 0.34–700 Torr of  $\text{O}_2$ .  $\text{N}_2$  was added to reach the desired total pressure of 0.38–940 Torr at  $296 \pm 2$  K.



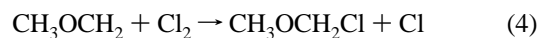
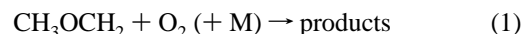
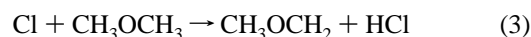
Loss of dimethyl ether and formation of products were monitored by Fourier transform infrared spectroscopy using an infrared path length of 27 m and a resolution of  $0.25 \text{ cm}^{-1}$ . Infrared spectra were derived from 32 coadded interferograms. Reference spectra were obtained by expanding known volumes of reference materials into the long path length cell at appropriate total pressures. Products were identified and quantified by fitting reference spectra of the pure compounds obtained at the appropriate total pressures to the observed product spectra using integrated absorption features over the following wavelength ranges (in  $\text{cm}^{-1}$ ): dimethyl ether, 900–1200; methyl formate, 1000–1100; methoxy methylhydroperoxide, 775–850 and 1700–1750; chlorodimethyl ether, 650–850 and 1200–1300;

formaldehyde, 1700–1800; formic acid, 1050–1150; CO, 2050–2250. All compounds were obtained from commercial vendors and used without further purification.

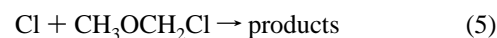
Four sets of experiments were performed. First, the kinetics of the  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  reaction were studied relative to the  $\text{CH}_3\text{OCH}_2 + \text{Cl}_2$  reaction as a function of total pressure. Second, the product distribution following the reaction of  $\text{CH}_3\text{OCH}_2$  radicals with  $\text{O}_2$  was studied over the pressure range 0.38–700 Torr. Third, the products of DME oxidation at 2, 5, and 700 Torr total pressures in the presence of a large excess of  $^{13}\text{CH}_3\text{OH}$ , and hence  $\text{HO}_2$  radicals, were studied. Finally, the apparent photolysis rate of  $\text{Cl}_2$  (calculated by the loss of DME) was measured at 2 and 700 Torr total pressure.

## 3. Results

**3.1. Relative Rate Study of  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  vs  $\text{CH}_3\text{OCH}_2 + \text{Cl}_2$ .** To study the rate constant ratio,  $k_1/k_4$ , mixtures of 10–31 mTorr of DME, 28–234 mTorr  $\text{Cl}_2$ , and 0.34–2.5 Torr  $\text{O}_2$  with  $\text{N}_2$  added to a total pressure of 0.38–940 Torr were subject to UV irradiation. The following reactions are important in the mixture:



Reaction 4 is expected to be independent of total pressure and provides a convenient reference for determining the pressure dependence of  $k_1$ . The fraction of the  $\text{CH}_3\text{OCH}_2$  radicals that react with  $\text{Cl}_2$ ,  $Y_{\text{DMECl}}$ , was determined by measuring the formation of  $\text{CH}_3\text{OCH}_2\text{Cl}$  ( $\Delta\text{DMECl}$ ) relative to the loss of DME ( $\Delta\text{DME}$ ). Hence,  $Y_{\text{DMECl}} = \Delta\text{DMECl}/\Delta\text{DME} = k_4[\text{Cl}_2]/(k_1[\text{O}_2] + k_4[\text{Cl}_2])$ . The measured yield of  $\text{CH}_3\text{OCH}_2\text{Cl}$  needs a small correction to account for loss of  $\text{CH}_3\text{OCH}_2\text{Cl}$  via reaction 5:

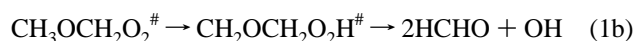
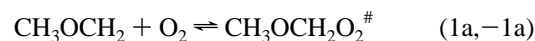


The rate constants for reactions 5 and 3 are  $k_5 = 2.9 \times 10^{-11}$  and  $k_3 = 1.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>4</sup> Conversion of DME was in the range 0–59%, and the corrections applied to  $Y_{\text{DMECl}}$  were <7%.

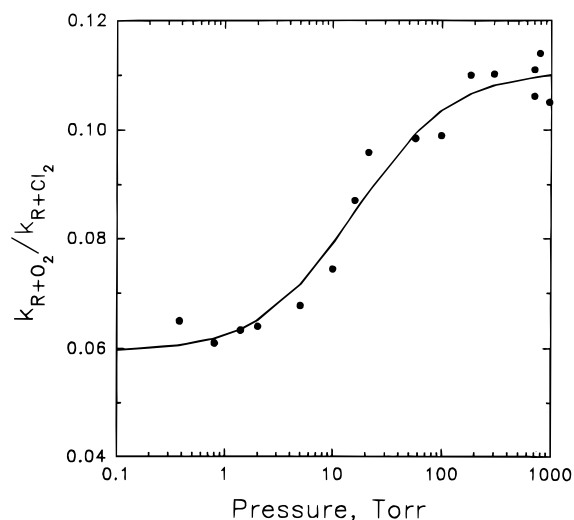
$k_1/k_4$  can then be calculated from eq 1:

$$k_1/k_4 = (1 - Y_{\text{DMECl}})[\text{Cl}_2]/(Y_{\text{DMECl}}[\text{O}_2]) \quad (1)$$

The results are shown in Figure 1. As expected,  $k_1/k_4$  approaches a high-pressure limit at pressures above 100 Torr and falls off below 100 Torr total pressure. It is interesting to note that  $k_1/k_4$  does not approach zero at low pressures. This behavior can be explained if reaction 1 proceeds via a complex that decomposes via two pathways, either to reform the reactants or to give other products. We show later that these “other products” are formaldehyde and OH radicals. The reactions involved in the formation and decomposition of the complex,  $\text{CH}_3\text{OCH}_2\text{O}_2^\#$ , are



At high pressures the rate constant for the reaction of  $\text{CH}_3\text{OCH}_2$



**Figure 1.**  $k_1/k_4$  vs total pressure. The smooth line is a fit to the data using a modified Lindemann mechanism (eq II). See text for details.

$\text{OCH}_2$  radicals with  $\text{O}_2$  equals  $k_{1a}$ , since all  $\text{CH}_3\text{OCH}_2\text{O}_2^\#$  radicals are quenched by the third body “M”, mainly  $\text{O}_2$  and  $\text{N}_2$  (reaction 1c), and the peroxy radical,  $\text{CH}_3\text{OCH}_2\text{O}_2$ , is formed. As the total pressure is decreased, not all of the  $\text{CH}_3\text{OCH}_2\text{O}_2^\#$  radicals are quenched and the rate constant ratio  $k_1/k_4$  decreases. At the low-pressure limit none of the  $\text{CH}_3\text{OCH}_2\text{O}_2^\#$  radicals are quenched; however, because of intramolecular hydrogen transfer in the excited  $\text{CH}_3\text{OCH}_2\text{O}_2^\#$  radical, the overall rate constant  $k_1$  does not drop to zero at zero total pressure. Hydrogen transfer in  $\text{CH}_3\text{OCH}_2\text{O}_2^\#$  is expected to proceed via a six-membered ring transition state.

Reactions 1a–1c can be viewed as a modified Lindemann mechanism. The overall reaction of  $\text{CH}_3\text{OCH}_2$  radicals with  $\text{O}_2$  proceeds via two pathways to give either the peroxy radical  $\text{CH}_3\text{OCH}_2\text{O}_2$  ( $\text{RO}_2$ ) or other products (prod). Hence,

$$-d[\text{CH}_3\text{OCH}_2]/dt = d[\text{RO}_2]/dt + d[\text{prod}]/dt = k_1[\text{CH}_3\text{OCH}_2][\text{O}_2]$$

$$d[\text{RO}_2]/dt = k_{\text{RO}_2}[\text{CH}_3\text{OCH}_2][\text{O}_2] = k_{1c}[\text{M}][\text{RO}_2^\#]$$

$$d[\text{prod}]/dt = k_{\text{prod}}[\text{CH}_3\text{OCH}_2][\text{O}_2] = k_{1b}[\text{RO}_2^\#]$$

Applying a steady state analysis for  $\text{RO}_2^\#$  gives

$$k_{\text{RO}_2} = k_{1a}k_{1c}[\text{M}]/(k_{-1a} + k_{1b} + k_{1c}[\text{M}])$$

$$k_{\text{prod}} = k_{1a}k_{1b}/(k_{-1a} + k_{1b} + k_{1c}[\text{M}])$$

Defining  $k_{\text{RO}_2,0} = k_{1a}k_{1c}/(k_{-1a} + k_{1b})$  and  $k_{\text{RO}_2,\infty} = k_{1a}$ , we can express the effective second-order rate constant for the formation of  $\text{RO}_2$  radicals at any given pressure,  $k_{\text{RO}_2}$ , in terms of the limiting low- and high-pressure rate constants,  $k_{\text{RO}_2,0}$  and  $k_{\text{RO}_2,\infty}$ :

$$k_{\text{RO}_2} = \frac{\{k_{1a}k_{1c}[\text{M}]/(k_{-1a} + k_{1b})\}/\{1 + k_{1a}k_{1c}[\text{M}]/(k_{1a}(k_{-1a} + k_{1b}))\}}{1 + k_{\text{RO}_2,0}[\text{M}]/k_{\text{RO}_2,\infty}}$$

Similarly, by definition of the rate constant for formation of “products” (formaldehyde and OH radicals) in the low-pressure

limit,  $k_{\text{prod},0} = k_{1a}k_{1b}/(k_{-1a} + k_{1b})$ , it follows that

$$k_{\text{prod}} = \frac{\{k_{1a}k_{1b}/(k_{-1a} + k_{1b})\}/\{1 + k_{1a}k_{1c}[\text{M}]/(k_{1a}(k_{-1a} + k_{1b}))\}}{1 + k_{\text{RO}_2,0}[\text{M}]/k_{\text{RO}_2,\infty}}$$

Equation II,

$$k_1/k_4 = k_{\text{RO}_2}/k_4 + k_{\text{prod}}/k_4 \quad (\text{II})$$

was fitted to the data in Figure 1 with  $k_{\text{prod},0}/k_4$ ,  $k_{\text{RO}_2,0}/k_4$ , and  $k_{\text{RO}_2,\infty}/k_4$  as parameters. The fit is shown as the smooth line through the data in Figure 1. As seen from Figure 1, the experimental data are well fitted by eq II. The best fit was obtained using  $k_{\text{prod},0}/k_4 = 0.059 \pm 0.005$ ,  $k_{\text{RO}_2,0}/k_4 = 0.0069 \pm 0.0032 \text{ Torr}^{-1} = (2.1 \pm 1.0) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$ , and  $k_{\text{RO}_2,\infty}/k_4 = 0.111 \pm 0.004$ .

Two absolute measurements of the rate constant for reaction 1 have been reported. Masaki et al.<sup>13</sup> measured  $k_1$  at 0.8–8 Torr total pressure and 298 K using a laser flash photolysis-mass spectrometry absolute technique. Masaki et al.<sup>13</sup> reported  $k_1 = (6.5 \pm 0.7) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  independent of total pressure over the pressure range studied. We also find that  $k_1$  is independent of total pressure below 6 Torr. Sehested et al.<sup>14</sup> measured  $k_1$  at 296 K at 1 bar total pressure using pulse radiolysis transient UV absorption spectroscopy and report  $k_1 = (1.09 \pm 0.05) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . The ratio of the absolute rate constants determined by Masaki et al.<sup>13</sup> at low pressure and by Sehested et al.<sup>14</sup> at high pressure is  $0.59 \pm 0.07$ . This is in good agreement with the ratio of the average of the relative rate data below 8 Torr total pressure,  $0.064 \pm 0.05$ , and the high-pressure limit determined in this study,  $0.111 \pm 0.004$ ,  $k_1(0-8 \text{ Torr})/k_{\text{RO}_2,\infty} = 0.58 \pm 0.05$ . Using the values for  $k_1$  of Masaki et al.<sup>13</sup> and Sehested et al.,<sup>14</sup>  $k_1(0-8 \text{ Torr}) = 0.064 \pm 0.005$ , and  $k_{\text{RO}_2,\infty}/k_4 = 0.111 \pm 0.004$ , we calculate  $k_4 = (1.02 \pm 0.14) \times 10^{-10}$  and  $k_4 = (0.98 \pm 0.06) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , respectively. We choose  $k_4 = (1.00 \pm 0.16) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , which is the average of two  $k_4$  values with an uncertainty that encompasses the extremes of the error limits of the individual determinations.

It is interesting to compare our result for  $k_4$  with the large kinetic data base for reactions of alkyl radicals with  $\text{Cl}_2$ . Rate constants at 298 K for such reactions are typically in the range  $(1-50) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .<sup>15</sup> For reasons that are unclear, the  $\text{CH}_3\text{OCH}_2$  radical displays an unusually high reactivity toward  $\text{Cl}_2$ .

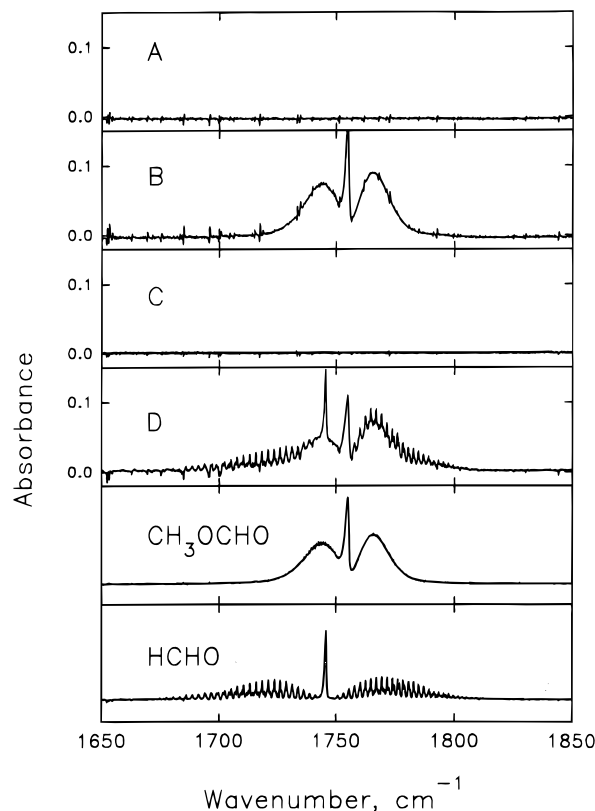
**3.2. Product Study of  $\text{CH}_3\text{OCH}_2 + \text{O}_2$ .** Six experiments were carried out to study the products of dimethyl ether oxidation as a function of total pressure. The initial conditions and the results are given in Table 1. In each experiment, a  $\text{CH}_3\text{OCH}_3/\text{Cl}_2/\text{O}_2/\text{N}_2$  mixture was subject to two to six successive periods of irradiation, each of 4–30 s duration. After each irradiation the reaction mixture was analyzed using FTIR spectroscopy.

Parts A and B of Figure 2 show IR spectra acquired before and after irradiation of a mixture of 23 mTorr of dimethyl ether, 23 mTorr of  $\text{Cl}_2$ , and 9.9 Torr of  $\text{O}_2$  in 690 Torr of  $\text{N}_2$  (experiment 6). Parts C and D of Figure 2 show IR spectra acquired before and after irradiation of a mixture of 23.1 mTorr of dimethyl ether and 23 mTorr of  $\text{Cl}_2$  in 10.4 Torr of  $\text{O}_2$  (experiment 5). The loss of dimethyl ether was 2.89 mTorr from spectrum A to B of Figure 2 and 2.77 mTorr from C to D. Reference spectra of methyl formate and formaldehyde are shown in the bottom panels of Figure 2. It is easily seen from the product spectra in parts B and D of Figure 2 that different products are observed at different total pressures. The product

**TABLE 1: Product Yields<sup>a</sup> Following the Irradiation of CH<sub>3</sub>OCH<sub>3</sub>/Cl<sub>2</sub>/O<sub>2</sub>/N<sub>2</sub> at 0.38–700 Torr Total Pressure**

set	[DME] <sup>b</sup>	[O <sub>2</sub> ] <sup>c</sup>	[N <sub>2</sub> ] <sup>c</sup>	[Cl <sub>2</sub> ] <sub>0</sub> <sup>b</sup>	P <sub>tot</sub> <sup>e</sup>	Y(CH <sub>3</sub> OCHO) %	Y(CH <sub>3</sub> OCH <sub>2</sub> OOH) %	Y(HCHO) %	Y(HCOOH) %	Y(CO) %
1	10.3	0.36	0	10.3	0.38	4 ± 2		181 ± 15		22 ± 4
2	10.4	1.06	0	10.4	1.08	6 ± 2		185 ± 20		14 ± 9
3	10.4	1.64	0	10.4	1.66	11 ± 2		173 ± 32		13 ± 5
4	21.8	5.7	0	15.4	5.7	32 ± 7	7 ± 2	120 ± 8		20 ± 8
5	23.1	10.4	0	23.0	10.4	42 ± 4	14 ± 3	89 ± 10	2 ± 2	6 ± 3
6	23.0	9.9	690	23.0	700	67 ± 2	30 ± 5			
7 <sup>d</sup>	29.6	1.2	699	15.8	700	88 ± 6		<1.9		
8 <sup>d</sup>	33.8	120	580	213.0	700	96 ± 20		<2		

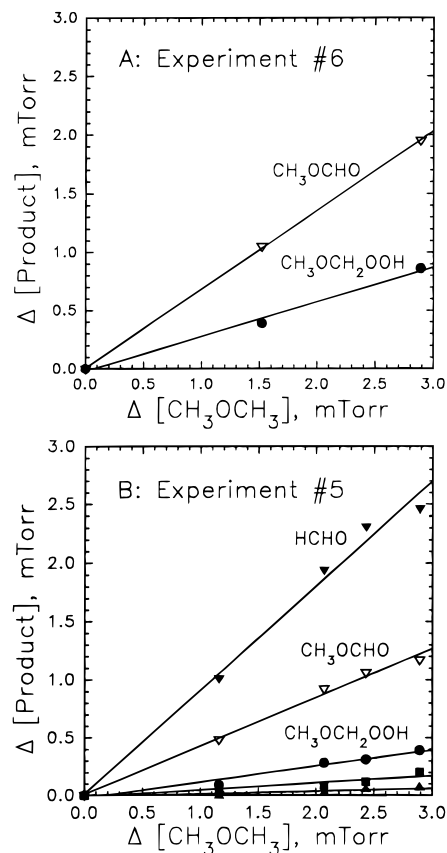
<sup>a</sup> Molar yields relative to CH<sub>3</sub>OCH<sub>3</sub> loss corrected for formation of CH<sub>3</sub>OCH<sub>2</sub>Cl. <sup>b</sup> Concentrations in units of mTorr. <sup>c</sup> Concentrations in units of Torr. <sup>d</sup> NO present in 15 mTorr concentration. <sup>e</sup> Total pressure in units of Torr.



**Figure 2.** IR spectra before (A) and after (B) irradiation of a mixture of 23 mTorr of DME, 23 mTorr of Cl<sub>2</sub>, and 9.9 Torr of O<sub>2</sub> with N<sub>2</sub> added to 700 Torr total pressure. (C) and (D) show IR spectra before and after irradiation of a mixture of 23.1 mTorr of DME, 23 mTorr of Cl<sub>2</sub>, and 10.4 Torr of O<sub>2</sub>. Reference spectra of methyl formate and formaldehyde are given in the bottom panels. See text for details.

observed in Figure 2B is methyl formate. Methyl formate and methoxy methylhydroperoxide were the only products observed in experiment 6. The yields of methyl formate and methoxy methylhydroperoxide were 1.95 and 0.86 mTorr, respectively. The product spectrum in Figure 2D shows that methyl formate and formaldehyde are formed at 10.4 Torr total pressure (experiment 5). The yield of methyl formate was 1.17 mTorr while that of HCHO was 2.46 mTorr. Examination of other regions of the product spectrum showed that formic acid, methoxy methylhydroperoxide, and CO were also formed in the low-pressure experiments in yields of 0.07, 0.39, and 0.20 mTorr, respectively.

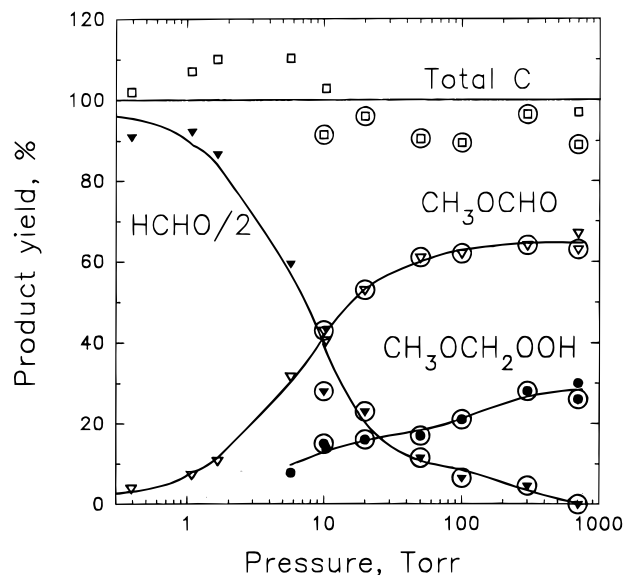
Parts A and B of Figure 3 show the observed yields of formaldehyde, CO, methyl formate, methoxy methylhydroperoxide, and formic acid plotted vs the loss of CH<sub>3</sub>OCH<sub>3</sub> in experiments 6 (700 Torr total pressure) and 5 (10.4 Torr total pressure), respectively. Linear least-squares analysis of the data in Figure 3A gives molar yields for methyl formate and methoxy methylhydroperoxide of 67 ± 2% and 30 ± 5%, respectively. Analysis of the data in Figure 3B gives molar yields for



**Figure 3.** Observed formation of methyl formate (▽), methoxy methylhydroperoxide (●), formaldehyde (▼), CO (■), and formic acid (▲) in experiment 6 (A) and experiment 5 (B).

formaldehyde, CO, methyl formate, methoxy methylhydroperoxide, and formic acid of 89 ± 10%, 6 ± 3%, 42 ± 4%, 14 ± 3%, and 2 ± 2%, respectively. These values are also reported in Table 1. With one exception (the HCHO yield plotted in Figure 4) all product yields in this paper are expressed as moles of product formed per mole of DME consumed. To calculate the carbon yield balance, allowance must be made for the fact that HCHO, CO, and HCOOH contain one carbon atom while methyl formate and methoxy methylhydroperoxide contain two. Quoted errors are 2 standard deviations and do not include potential systematic errors associated with uncertainties in the calibrations of the reference spectra. We estimate that potential systematic errors could contribute an additional 10% range.

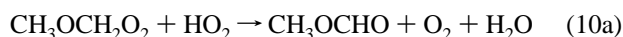
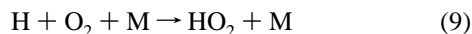
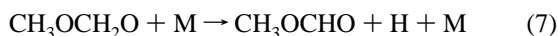
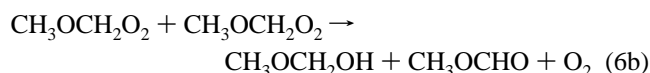
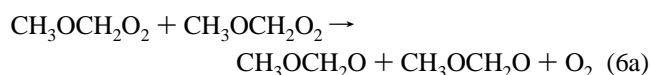
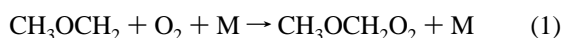
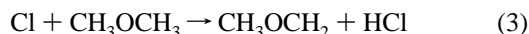
Figure 4 shows the yields of formaldehyde, methyl formate, and methoxy methylhydroperoxide as a function of the total pressure. The yields and experimental conditions are also shown in Table 1. The product yields are corrected for CH<sub>3</sub>OCH<sub>2</sub>Cl formed via reaction 4. The corrections were small (<10%). The product data determined by Jenkin et al.<sup>4</sup> are also shown in Figure 4. Clearly, there is good agreement between the data obtained here and those reported by Jenkin et al.<sup>4</sup> The total



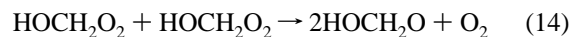
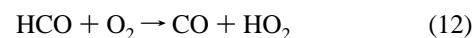
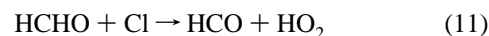
**Figure 4.** Molar yields (relative to the dimethyl ether loss) of methyl formate ( $\nabla$ ), methoxy methylhydroperoxide ( $\bullet$ ), and the molar yield of formaldehyde ( $\blacktriangledown$ ) divided by 2 vs total pressure. The total carbon yield is shown with hollow squares. Results reported previously by Jenkin et al.<sup>4</sup> are given by the symbols enclosed by large circles. The smooth lines are fits to polynomial expressions to aid visual inspection of the data.

product yields are also shown in Figure 4 and are, within the experimental uncertainties ( $\sim 10\%$ ), indistinguishable from 100%.

At 700 Torr total pressure the  $C_2$  compounds, methyl formate and methoxy methylhydroperoxide, are the only observable products of dimethyl ether oxidation. This can be explained by the following reactions:

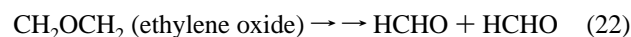
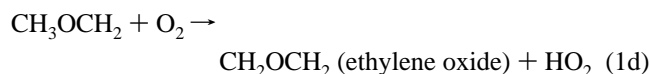
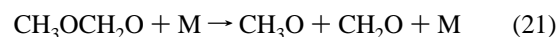
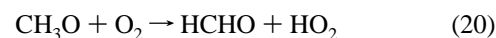
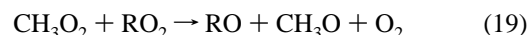
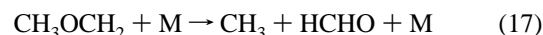


Reaction 6 proceeds via two channels with  $k_{6a}/(k_{6a} + k_{6b}) = 0.7 \pm 0.1$ .<sup>4</sup> The yield of  $\text{CH}_3\text{OCH}_2\text{OH}$  in this system is  $< 15\%$ .<sup>4</sup> At lower pressures the  $C_1$  products, formaldehyde, CO, and HCOOH, are the dominant products of the oxidation of dimethyl ether. At 0.38 Torr total pressure the yield of methyl formate is only 4% while formaldehyde is observed in a yield that accounts for greater than 90% of the loss of DME. CO and HCOOH are seen in small yields at low total pressure. Their formation can be rationalized by the following reactions<sup>16,17</sup>:

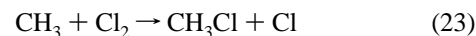


As seen from Figure 4, the yield of  $\text{CH}_3\text{OCH}_2\text{OOH}$  drops with decreasing pressure. There was no detectable  $\text{CH}_3\text{OCH}_2\text{OOH}$  product ( $< 5\%$  yield) for experiments conducted below 2 Torr. There are two reasons for the declining yield of  $\text{CH}_3\text{OCH}_2\text{OOH}$ . First, there is the decreased yield of  $\text{CH}_3\text{OCH}_2\text{O}$  radicals at low pressure. Second, with low total pressures of  $\text{O}_2$  diluent, H atom elimination rather than reaction with  $\text{O}_2$  becomes an important fate of  $\text{CH}_3\text{OCH}_2\text{O}$  radicals.<sup>4</sup> At low total pressures H atoms react with  $\text{Cl}_2$ , thereby avoiding  $\text{HO}_2$  radical formation. Without  $\text{HO}_2$  radicals there can be no  $\text{CH}_3\text{OCH}_2\text{OOH}$  formation.

There are four possible sources of the large yield of formaldehyde observed at low pressures. The formaldehyde is formed from the thermal decomposition of  $\text{CH}_3\text{OCH}_2$  radicals (reactions 17–20), from the decomposition of the alkoxy radical,  $\text{CH}_3\text{OCH}_2\text{O}$  (reaction 21), from a bimolecular channel of reaction 1 (to give ethylene oxide (reaction 1d) followed by conversion of the ethylene oxide into formaldehyde by some (unknown) mechanism (reaction 22), or from the reaction of  $\text{CH}_3\text{OCH}_2$  with  $\text{O}_2$  via reaction 1b:

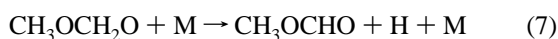


Two pieces of information show that reaction 17 is not important in the present reaction system. First, the thermal decomposition of  $\text{CH}_3\text{OCH}_2$  radicals has been studied by Louck and Laidler<sup>18</sup> and Sehested et al.<sup>14</sup> The following expression was derived for the high-pressure limit of the thermal decomposition of  $\text{CH}_3\text{OCH}_2$  radicals:  $k_{14} = 1.6 \times 10^{13} \exp(-12832/T) \text{ s}^{-1}$ .<sup>14,18</sup> From this expression it can be calculated that the lifetime of  $\text{CH}_3\text{OCH}_2$  radicals at 296 K is 4.9 days and that reaction 17 is not important in the present chemical system. Second, no  $\text{CH}_3\text{Cl}$  was observed in the relative rate experiments described in section 3.1. If  $\text{CH}_3$  radicals were produced in reaction 17, then  $\text{CH}_3\text{Cl}$  formed by reaction 23 would be a major product in the reaction system where  $[\text{O}_2]/[\text{Cl}_2] \approx 10$ .



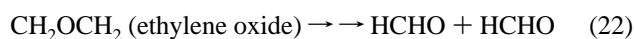
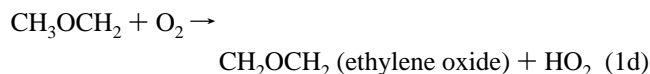
At 5 Torr total pressure the rate constant ratio  $k_{18}/k_{23} = 0.05$ <sup>19</sup> and  $k_{18}/k_{23}$  will decrease further at lower pressures. In a system where  $[O_2]/[Cl_2] \approx 10$  the main fate of methyl radicals formed in reaction 17 is formation of  $CH_3Cl$  via reaction 23. No  $CH_3Cl$  was observed in any of the experiments described in section 3.1. Hence, we conclude that reaction 17 is not important.

Decomposition of  $CH_3OCH_2O$  radicals via C–O bond cleavage is another possible source of formaldehyde. The decomposition rate of  $CH_3OCH_2O$  radicals is expected to be greatest at high pressures. To provide insight into the importance of the thermal decomposition of  $CH_3OCH_2O$  radicals, two experiments were performed where mixtures of DME/ $Cl_2$ /NO with either 1.2 or 140 Torr of oxygen with  $N_2$  added to 700 Torr total pressure were irradiated. Under such experimental conditions essentially all  $CH_3OCH_2$  radicals will be converted into  $CH_3OCH_2O_2$  radicals and thence to  $CH_3OCH_2O$  radicals. The experimental details are given in Table 1 (experiments 7 and 8). Methyl formate was the only observable product in experiments 7 and 8. An upper limit of 2% was established for the HCHO yield. This result shows that the fate of  $CH_3OCH_2O$  radicals is elimination of a H atom via reaction 7, or reaction with  $O_2$ , or both.



Since thermal decomposition of  $CH_3OCH_2O$  radicals via C–O bond cleavage is not important at 700 Torr total pressure and  $[O_2] = 1.2$  Torr, it cannot be important at the lower total pressures used for experiments 1–5 (see Table 1).

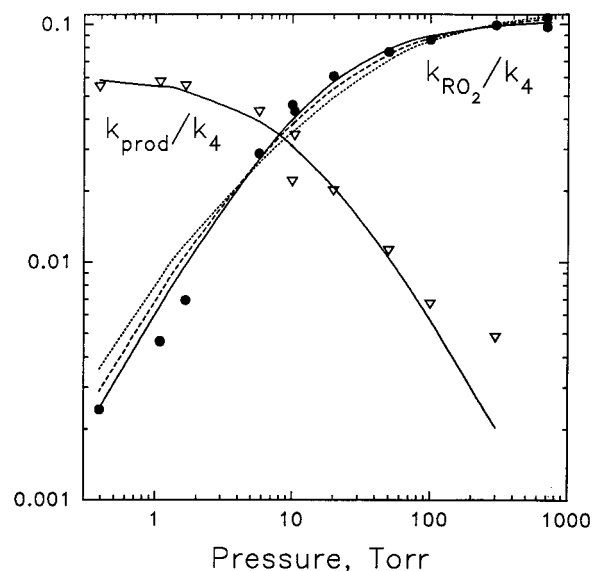
A direct hydrogen abstraction mechanism for reaction 1 followed by reaction 22 can be proposed as a source of formaldehyde at low pressures:



However, if the formation of formaldehyde and the nonzero intercept in Figure 1 were due to such a pressure independent, direct bimolecular channel of reaction 1, then inspection of Figure 1 reveals that reaction 1d would account for approximately half the overall rate constant at 700 Torr. At pressures below 1 Torr the reaction of  $CH_3OCH_2$  radicals with  $O_2$  results in the conversion of essentially all  $CH_3OCH_2$  radicals into formaldehyde. If reaction 1d was the explanation of the formaldehyde formation and the nonzero intercept in Figure 1 then we would expect that at 700 Torr total pressure approximately 50% of  $CH_3OCH_2$  radicals would be converted into formaldehyde. In contrast, the formaldehyde yield from dimethyl ether oxidation at 700 Torr total pressure is <2%. Hence, we conclude that reaction 1d is unimportant.

Finally, we need to consider the possible formation of HCHO directly in the reaction of  $CH_3OCH_2$  radicals with  $O_2$ . As discussed in the previous section, the mechanism proposed for reaction 1, which includes reactions 1a, 1b, and 1c, explains the pressure dependence of  $k_1$  very well. We will show below that the reaction mechanism also explains the pressure dependence of the product distribution shown in Figure 4. Assuming that all thermalized peroxy radicals react to give  $C_2$  products, methyl formate or methoxy methylhydroperoxide, the fraction of the  $CH_3OCH_2$  radicals reacting with  $O_2$  that give the peroxy radical,  $CH_3OCH_2O_2$ , is given by

$$\alpha = k_{RO_2}/k_1 \quad (III)$$



**Figure 5.** Plot of the combined yield of the  $C_2$  products, methyl formate, and methoxy methylhydroperoxide  $\times k_1/k_4$  ( $k_{RO_2}/k_4$  (●)) and the  $C_1$  products, formaldehyde, HCOOH, and CO  $\times k_1/k_4$  ( $k_{prod}/k_4$  (▽)) vs the total pressure. The smooth, dashed, and dotted lines are fits using  $F_c = 1$  (Lindemann expression), 0.8, and 0.6, respectively. See text for details.

where  $k_{RO_2}$  and  $k_1$  are the rate constants for the formation of  $CH_3OCH_2O_2$  radicals and the overall rate constant for reaction 1, respectively. Similarly, the fraction of reaction 1 that gives formaldehyde and OH radical is given by

$$\beta = k_{prod}/k_1 \quad (IV)$$

where  $k_{prod}$  is the rate constant for the formation of formaldehyde and OH radicals.  $k_{RO_2}/k_4$  and  $k_{prod}/k_4$  can be calculated directly from the experimental data by multiplying the fraction of the products that are  $C_1$  and  $C_2$  products by the values of  $k_1/k_4$  derived in section 3.1. Figure 5 shows the resulting values of  $k_{RO_2}/k_4$  and  $k_{prod}/k_4$  calculated by multiplying the product data given in Figure 4 by appropriate values of  $k_1/k_4$  derived from the fit through the data in section 3.1. These two data sets can be fitted by the following expressions derived in section 3.1:

$$k_{RO_2}/k_4 = k_{RO_2,0}[M]/\{k_4(1 + k_{RO_2,0}[M]/k_{RO_2,\infty})\} \quad (V)$$

$$k_{prod}/k_4 = k_{prod,0}/\{k_4(1 + k_{RO_2,0}[M]/k_{RO_2,\infty})\} \quad (VI)$$

using  $k_{RO_2,0}/k_4$  and  $k_{RO_2,\infty}/k_4$  (eq V) and  $k_{prod,0}/k_4$  and  $k_{RO_2,\infty}/k_4$  (eq VI) as parameters. The fits are given as solid lines in Figure 5. The parameters obtained from the fits were  $k_{RO_2,0}/k_4 = (6.45 \pm 0.92) \times 10^{-3} \text{ Torr}^{-1} = (1.97 \pm 0.28) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$  and  $k_{RO_2,\infty}/k_4 = 0.104 \pm 0.007$  ( $k_{RO_2}$  fit) and  $k_{prod,0}/k_4 = (6.6 \pm 0.9) \times 10^{-2}$  and  $k_{RO_2,0}/k_{RO_2,\infty} = (8.4 \pm 3.2) \times 10^{-2} \text{ Torr}^{-1} = (2.6 \pm 1.0) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$  ( $k_{prod}$  fit). These values are consistent with the rate constant ratios obtained in section 3.1. We choose to report the average of the values of  $k_{RO_2,\infty}/k_4$  and  $k_{prod,0}/k_4$  determined in section 3.1 and in this section. Hence,  $k_{RO_2,\infty}/k_4 = 0.108 \pm 0.004$  and  $k_{prod,0}/k_4 = (6.3 \pm 0.5) \times 10^{-2}$ ; uncertainties were calculated by normal error propagation methods. For  $k_{RO_2,0}/k_4$  we choose to report the more precise value determined in this section,  $k_{RO_2,0}/k_4 = (1.97 \pm 0.28) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$ .

As a check of the validity of the use of a modified Lindemann mechanism to analyze the data obtained in this work, the  $k_{RO_2}/k_4$  data in Figure 5 were also analyzed by using a Troe type expression:

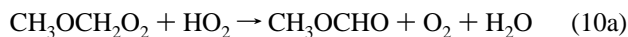
$$k_{\text{RO}_2}/k_4 = k_{\text{RO}_2,0}[\text{M}]/(k_4(1 + k_{\text{RO}_2,0}[\text{M}]/k_{\text{RO}_2,\infty}))F_c^{(1+\log(k_{\text{RO}_2,0}[\text{M}]/k_{\text{RO}_2,\infty}))^{-1}} \quad (\text{VII})$$

where  $k_{\text{RO}_2,0} = k_{1a}k_{1c}/(k_{-1a} + k_{1b})$ ,  $k_{\text{RO}_2,\infty} = k_{1a}$ , and  $k_{\text{RO}_2}$  is the overall rate constant for  $\text{RO}_2$  formation.  $k_{\text{RO}_2,0}$ ,  $k_{\text{RO}_2,\infty}$ , and  $k_{\text{RO}_2}$  are also used in eq II and discussed in section 3.1. The Troe type expression (eq VII) describes the pressure dependence of a reaction system consisting of reactions 1a–c. Introducing the additional reaction 1b in the present chemical system should not alter the pressure dependence of  $k_{\text{RO}_2}$ . The fits to the data using eq VII and  $F_c = 0.6$  (dotted lines) and  $F_c = 0.8$  (dashed lines) are shown in Figure 5. The Troe expression (eq VII) is equal to the Lindemann expression (eq II) when  $F_c = 1$ . As seen from Figure 5, the fits using  $F_c = 1$  give the best representation of the  $k_{\text{RO}_2}/k_4$  data.

**3.3. Product Study of  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  in the Presence of  $^{13}\text{CH}_3\text{OH}$ .** As a part of this work, a product study of the oxidation of dimethyl ether in the presence of a large excess of  $^{13}\text{CH}_3\text{OH}$  was performed at 2, 5, and 700 Torr total pressure. The initial conditions and the results are given in Table 2. Chlorine-initiated oxidation of methanol gives  $\text{HO}_2$  radicals:



$\text{HO}_2$  radicals react with  $\text{CH}_3\text{OCH}_2\text{O}_2$  radicals via two reaction pathways:



All experiments were conducted using an initial concentration ratio of  $[^{13}\text{CH}_3\text{OH}]/[\text{DME}] = 10$ . This ratio was selected because previous experiments<sup>5</sup> have shown that under such conditions the sole fate of  $\text{CH}_3\text{OCH}_2\text{O}_2$  radicals is reaction with  $\text{HO}_2$  radicals.  $^{13}\text{CH}_3\text{OH}$  was used as opposed to  $\text{CH}_3\text{OH}$  in this study to avoid formation of  $\text{H}^{12}\text{CHO}$  from methanol in the system. By use of  $^{13}\text{CH}_3\text{OH}$ , dimethyl ether oxidation is the only source of  $\text{H}^{12}\text{CHO}$ .

As seen from Tables 1 and 2, the yields of formaldehyde and  $\text{C}_2$  products (methyl formate and methoxy methylhydroperoxide) obtained with  $^{13}\text{CH}_3\text{OH}$  present are indistinguishable from those obtained without methanol present in the chamber apart from the yields of  $\text{C}_2$  products reported at 2.2 Torr total pressure. The yield of  $\text{C}_2$  products with  $^{13}\text{CH}_3\text{OH}$  present is  $29 \pm 6\%$  (2.2 Torr total pressure). The yields of  $\text{C}_2$  products reported in Table 1 are  $11 \pm 2\%$  at 1.66 Torr and  $32 \pm 7\%$  at 5.7 Torr total pressure. This apparent discrepancy may be due to a very high third-body efficiency of methanol, which would increase the yield of  $\text{C}_2$  products at the expense of formaldehyde. We therefore believe that the yields of  $\text{C}_1$  and  $\text{C}_2$  products from dimethyl ether oxidation with and without  $^{13}\text{CH}_3\text{OH}$  are indistinguishable.

The relative yields of methyl formate and the methoxy methylhydroperoxide with methanol present in the system are consistent with those reported by Wallington et al.<sup>5</sup> of  $40 \pm 4\%$  methyl formate and  $53 \pm 8\%$  methoxy methylhydroperoxide.

It is interesting to note that the yield of formaldehyde from dimethyl ether oxidation is not affected by the presence of  $^{13}\text{CH}_3\text{OH}$ .  $\text{CH}_3\text{OCH}_2\text{O}_2$  radicals are known to be rapidly scavenged by  $\text{HO}_2$  radicals in the system to give  $\text{CH}_3\text{OCHO}$  and  $\text{CH}_3\text{OCH}_2\text{OOH}$ .<sup>5</sup> The insensitivity of the  $\text{HCHO}$  yield to the presence of  $\text{CH}_3\text{OH}$  suggests that  $\text{HCHO}$  is formed before  $\text{CH}_3\text{OCH}_2\text{O}_2$  radicals are produced. As discussed above, the

thermal decomposition of  $\text{CH}_3\text{OCH}_2$  radicals is too slow to be of any importance under the present experimental conditions. Therefore, the experiments conducted in the presence of a large excess of methanol suggest that reaction 1 is indeed the source of formaldehyde.

**3.4. Apparent Photolysis Rate of  $\text{Cl}_2$  at 2, 5, and 700 Torr Total Pressure.** The apparent photolysis rate of  $\text{Cl}_2$ , as measured from the rate of dimethyl ether loss, was determined for three sets of initial experimental conditions. During these experiments only 4 out of the 22 blacklamps were used to photolyze molecular chlorine. The initial concentrations were  $[\text{DME}] = 10$  mTorr,  $[\text{Cl}_2] = 33$  mTorr, and  $[\text{O}_2] = 2$  (experiment 1), 2 (experiment 2), or 140 (experiment 3) Torr with  $\text{N}_2$  added to 700 Torr total pressure in experiments 2 and 3. The photolysis rates were calculated by eq VIII:

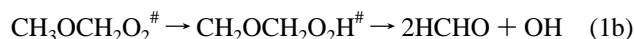
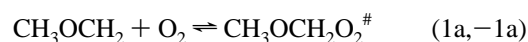
$$J_{\text{Cl}_2} = (\Delta[\text{CH}_3\text{OCH}_3] - \Delta[\text{CH}_3\text{OCH}_2\text{Cl}]) / (2[\text{Cl}_2]\Delta t) \quad (\text{VIII})$$

where  $\Delta[\text{CH}_3\text{OCH}_3]$  is the observed loss of dimethyl ether,  $\Delta[\text{CH}_3\text{OCH}_2\text{Cl}]$  is the observed formation of  $\text{CH}_3\text{OCH}_2\text{Cl}$ ,  $\Delta t$  is the irradiation time, and  $[\text{Cl}_2]$  the initial chlorine concentration. The photolysis rates were determined to be  $(1.05 \pm 0.10) \times 10^{-3} \text{ s}^{-1}$  (experiment 1),  $(3.8 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$  (experiment 2), and  $(3.8 \pm 0.2) \times 10^{-4} \text{ s}^{-1}$  (experiment 3). As expected, the apparent photolysis rate of  $\text{Cl}_2$  in 700 Torr of air (experiment 3) is the same as that measured in 2 Torr of oxygen and 698 Torr of  $\text{N}_2$  (experiment 2). However, the apparent photolysis rate in 2 Torr total pressure of  $\text{O}_2$  (experiment 1) is  $2.8 \pm 0.3$  times higher than those observed at 700 Torr total pressure (experiments 2 and 3). This observation suggests that a chain reaction is operating at low pressures (i.e., more than one molecule of  $\text{CH}_3\text{OCH}_3$  is consumed for each Cl atom formed in the system). In light of the reaction mechanism proposed for the reaction of  $\text{CH}_3\text{OCH}_2$  radicals with  $\text{O}_2$  in the previous sections, it seems reasonable to conclude that the apparent enhancement of the  $\text{Cl}_2$  photolysis rate can be ascribed to additional loss of  $\text{CH}_3\text{OCH}_3$  via reaction with OH radicals produced in reaction 1b.

As an additional check on this chemical system, the concentration of HCl after 25 s irradiation of reaction mixture 1 was compared with that in reaction mixture 3 after 55 s irradiation. The loss of dimethyl ether in these two experiments were comparable; 1.55 mTorr in experiment 1 and 1.34 mTorr in experiment 3. The yield of HCl in reaction mixture 1 was found to be  $0.55 \pm 0.20$  times that in reaction mixture 3. Hence, the HCl yield per dimethyl ether molecule consumed in experiment 1 is  $0.48 \pm 0.17$  of that in experiment 3. This result is entirely consistent with the magnitude of the enhancement of the apparent  $\text{Cl}_2$  photolysis rate.

#### 4. Discussion

The experimental observations presented in sections 3.1–3.4 constitute a large body of self-consistent kinetic and product data that show that the reaction of  $\text{CH}_3\text{OCH}_2$  radicals with  $\text{O}_2$  proceeds via the formation of an excited complex ( $\text{CH}_3\text{OCH}_2\text{O}_2^\#$ ). This complex has one of three fates: decomposition back into reactants, collisional stabilization to give thermalized  $\text{CH}_3\text{OCH}_2\text{O}_2$  radicals, or isomerization via intramolecular H-atom abstraction followed by decomposition to give two formaldehyde molecules and an OH radical:



**TABLE 2: Product Yields<sup>a</sup> Following the Irradiation of CH<sub>3</sub>OCH<sub>3</sub>/<sup>13</sup>CH<sub>3</sub>OH/Cl<sub>2</sub>/O<sub>2</sub> Mixtures**

set	[DME]/[ <sup>13</sup> CH <sub>3</sub> OH] <sup>b</sup>	[O <sub>2</sub> ] <sup>c</sup>	[N <sub>2</sub> ] <sup>c</sup>	[Cl <sub>2</sub> ] <sub>0</sub> <sup>b</sup>	Y(CH <sub>3</sub> OCHO) %	Y(CH <sub>3</sub> OCH <sub>2</sub> OOH) %	Y(HCHO) %	Y(CO) %
1	10.6/117	2.2	0	33	14 ± 1	15 ± 5	130 ± 14	9 ± 4
2	10.4/104	10.5	0	33	29 ± 3	42 ± 13	78 ± 12	
3	10.4/104	140	560	33	46 ± 6	56 ± 8		

<sup>a</sup> Molar yields relative to CH<sub>3</sub>OCH<sub>3</sub> loss corrected for formation of CH<sub>3</sub>OCH<sub>2</sub>Cl. <sup>b</sup> Concentrations in units of mTorr. <sup>c</sup> Concentrations in units of Torr.

In section 3.1 it was shown that the rate constant for reaction 1 is independent of total pressure below 2 Torr. In section 3.2 the products of reaction 1 were studied and it was shown that formaldehyde is the dominant product below 10 Torr. In section 3.3 the products of dimethyl oxidation were studied in the presence of a source of a large excess of HO<sub>2</sub> radicals such that any CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> radical would be scavenged by reaction with HO<sub>2</sub> radicals. The formaldehyde yield was insensitive to the presence of excess HO<sub>2</sub> radicals, suggesting that formaldehyde formation occurs before the formation of CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> radicals. This experiment provides evidence that formaldehyde is formed via reaction 1b. Finally, the apparent chlorine photolysis rate and the HCl yield were studied at 2 and 700 Torr total pressure. The apparent photolysis rate was enhanced by a factor of 2.8 ± 0.3, while the HCl yield was suppressed by a factor of 0.48 ± 0.17 at 2 Torr total pressure compared to 700 Torr. These observations are consistent with the formation of OH radicals in reaction 1b.

### 5. Implications for Atmospheric Chemistry

The atmospheric oxidation of dimethyl ether is initiated by reaction with OH radicals. The reaction of OH radicals with dimethyl ether gives CH<sub>3</sub>OCH<sub>2</sub> radicals whose sole fate is reaction with O<sub>2</sub>. The rate constant at 298 K for the reaction of OH radicals with dimethyl ether is 260 times (2.5 × 10<sup>-12</sup> / 9.6 × 10<sup>-15</sup>) that of reaction with CH<sub>3</sub>CCl<sub>3</sub>, which has an atmospheric lifetime of 5.7 years. Hence, the atmospheric lifetime of DME is approximately 8 days. We have shown herein that at 296 K the reaction of CH<sub>3</sub>OCH<sub>2</sub> radicals with O<sub>2</sub> proceeds via two channels to give either CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> radicals or HCHO and OH radicals. For pressures above ~10 Torr the formation of CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> radicals dominates, while for pressures less than ~10 Torr the formation of HCHO and OH radicals is dominant. Since the vast majority of the atmospheric oxidation of dimethyl ether occurs at pressures substantially above 10 Torr and with the reasonable assumption that the importance of reaction 1c does not decrease dramatically with temperature over the atmospherically relevant range 220–296 K, it follows that the vast majority of the dimethyl ether released to the atmosphere is oxidized via reaction 1c.

### 6. Implications for Combustion Chemistry

The mechanism for reaction 1 at 296 K found in this work may explain why DME is a good diesel fuel. By analogy with the formation of ethene from the reaction of ethyl radicals with O<sub>2</sub>,<sup>21</sup> it is expected that the relative importance of reaction 1b will increase with temperature because reaction 1c becomes reversible and multiple passes through reaction 1a become

possible. It is well-known that intramolecular hydrogen transfer is important in excited alkyl peroxy radicals at high temperatures (500–1000 °C).<sup>8</sup> Reaction 1b may be the major pathway for the reaction of CH<sub>3</sub>OCH<sub>2</sub> radicals with O<sub>2</sub> under compression–ignition conditions. If so, this might explain the high cetane number of dimethyl ether. In addition, the formation of formaldehyde during dimethyl ether combustion would explain the low particle emissions from diesel engines powered by DME. A study of the mechanism for reaction 1 at higher temperatures is necessary to determine the importance of reaction 1b in the ignition and combustion of dimethyl ether.

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