

Kinetic Studies of the Oxidation of Dimethyl Ether and Its Chain Reaction with Cl<sub>2</sub>

M. Matti Maricq,\* Joseph J. Szente, and John D. Hybl†

Research Laboratory, Ford Motor Company, P.O. Box 2053, Drop 3083, Dearborn, Michigan 48121

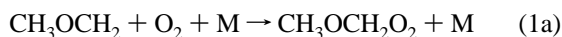
Received: March 17, 1997; In Final Form: May 6, 1997<sup>⊗</sup>

The reaction between dimethyl ether radicals and molecular oxygen proceeds along two distinct pathways at temperatures between 230 and 350 K. Above about 100 Torr total pressure the peroxy radical, CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub>, is predominantly formed. As the pressure is reduced, a channel leading to the formation of OH and two formaldehyde molecules becomes progressively more important. Real time kinetic measurements of these reactions are made using time-resolved UV spectroscopy to monitor CH<sub>3</sub>OCH<sub>2</sub> loss and CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> formation along with transient IR absorption to probe formaldehyde production. The OH radicals are identified via their UV spectrum. The reaction can be described via a modified Lindemann mechanism using the three parameters  $k_{\text{ro}2,\infty}$ ,  $k_{\text{ro}2,0}$ , and  $k_{\text{prod},0}$ , which represent the high- and low-pressure limits of the O<sub>2</sub> addition reaction and the low-pressure limit of the OH/formaldehyde channel. At 295 K they have values of  $(1.1 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ,  $(2.6 \pm 0.9) \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$ , and  $(6 \pm 2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , respectively. At  $P_{\text{tot}} = \sim 120$  Torr the reaction exhibits a negative temperature dependence with  $k_{\text{r}+\text{o}2} = (3.1_{-0.8}^{+1.0}) \times 10^{-12} \text{ e}^{(326 \pm 80)/T} \text{ cm}^3 \text{ s}^{-1}$ . Experiments in the absence of oxygen were performed to investigate the CH<sub>3</sub>OCH<sub>2</sub>-mediated chain reaction between chlorine and dimethyl ether. Analysis of time-resolved UV spectra reveals rate constants of  $k_{\text{r}+\text{cl}2} = (1.8_{-0.5}^{+0.7}) \times 10^{-11} \text{ e}^{(360 \pm 120)/T} \text{ cm}^3 \text{ s}^{-1}$  and  $k_{\text{r}+\text{r}} = (1.8_{-0.5}^{+0.6}) \times 10^{-11} \text{ e}^{(200 \pm 100)/T} \text{ cm}^3 \text{ s}^{-1}$ , respectively, for the chain propagation reaction between CH<sub>3</sub>OCH<sub>2</sub> and molecular chlorine and for the chain-terminating recombination reaction.

## Introduction

The oxidation of dimethyl ether is of interest on two counts: From the atmospheric chemistry perspective it is the simplest representative of the class of ether compounds, some of which (e.g. methyl *tert*-butyl ether, MTBE) find use as automotive fuel additives.<sup>1</sup> From the standpoint of combustion chemistry, dimethyl ether has been advanced, due to its high cetane number and low soot production, as an alternative, low-emissions, diesel fuel.<sup>2</sup> An interesting property of dimethyl ether is that its combustion is readily initiated by compression ignition; that is, it has a high cetane number. In contrast to other ethers the cetane number is very high (CN > 55), comparable, or even superior, to conventional diesel fuel.<sup>2</sup> Concomitantly, whereas other ethers, such as MTBE, find application as octane enhancers,<sup>1</sup> dimethyl ether exhibits a very low octane number and would function poorly in this regard.

A possible explanation for dimethyl ether's compression ignition propensity lies in its oxidation chemistry. Previous product studies of the chlorine atom initiated low-temperature oxidation of dimethyl ether revealed a dependence on total pressure;<sup>3</sup> as the pressure is lowered, formaldehyde is produced at the expense of CH<sub>3</sub>OCHO. This observation was explained by postulating two channels for the reaction between methoxymethyl radicals and oxygen,



the conventional oxygen addition reaction along with a bimolecular channel, both of which presumably proceed through an excited reaction complex, CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub>\*.

Verification of OH radical formation would have important implications with respect to the compression ignition of dimethyl ether, since this radical is an important reactive intermediate in the combustion process. Alkyl radical oxidation reactions are usually dominated by processes leading to the much less reactive hydroperoxy and organic peroxy radicals, until the temperature becomes sufficiently high to sustain combustion. If hydroxyl radicals are formed directly at lower temperature during the initial steps of dimethyl ether oxidation, they would attack the fuel in a catalytic fashion, providing a plausible mechanism for the facile initiation of combustion.

The time-resolved observations of OH and CH<sub>2</sub>O reported here furnish direct evidence for the proposed rearrangement/dissociation channel of the reaction between CH<sub>3</sub>OCH<sub>2</sub> and molecular oxygen. Kinetic data for this reaction are determined not only by following the loss of CH<sub>3</sub>OCH<sub>2</sub> with time but also by measuring the appearance of CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> and CH<sub>2</sub>O, producing a consistent picture of this reaction. Temperature and pressure dependent rate constants are presented for this reaction as well as for the chain reaction between CH<sub>3</sub>OCH<sub>2</sub> and Cl<sub>2</sub> and for the CH<sub>3</sub>OCH<sub>2</sub> recombination reaction. These data are compared to previous measurements on this system.

## Experimental Section

The kinetics of the reactions of CH<sub>3</sub>OCH<sub>2</sub> with itself, Cl<sub>2</sub>, and O<sub>2</sub> were interrogated using time-resolved UV spectroscopy<sup>4</sup> and transient infrared absorption,<sup>5</sup> both of which have been previously described. The former technique was used to probe the intermediate CH<sub>3</sub>OCH<sub>2</sub>, OH, and CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> radicals formed in these reactions as well as the loss of Cl<sub>2</sub>. Transient infrared absorption was used to monitor formaldehyde generation.

Time-resolved UV spectra are collected using a gated diode array spectrometer. Broad-band UV light from either a D<sub>2</sub> or Xe lamp propagates through the cell in a direction opposite to the photolysis beam, is dispersed by a monochromator, and impinges the array detector, which is gated to measure the

\* Author to whom correspondence is addressed.

† Present address: Department of Chemistry, University of Colorado, Boulder, CO 80309.

⊗ Abstract published in *Advance ACS Abstracts*, June 15, 1997.

transmitted light intensity at specified times 4–300  $\mu\text{s}$  after the photolysis pulse. At each delay time the recorded absorbance consists of contributions from each absorbing species weighted by its UV absorption spectrum and concentration; thus,

$$\text{Abs}(\lambda, t) = \sum_i I\sigma_i(\lambda) C_i(t) \quad (2)$$

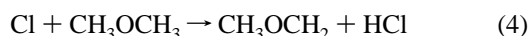
These spectra are subsequently deconvolved, using independently measured absorption cross sections for each species, to provide the time variation in the concentration of each absorbing species over the course of the reaction. In the present experiments these species include  $\text{CH}_3\text{OCH}_2$ ,  $\text{CH}_3\text{OCH}_2\text{O}_2$ ,  $\text{Cl}_2$ ,  $\text{CH}_3\text{OCH}_2\text{Cl}$ , and  $\text{CH}_3\text{OCH}_3$ ; however, the last two molecules exhibit nearly identical spectra over the 190–350 nm region investigated, and only their combined concentration change can be followed (the spectra are illustrated in Figure 1).

Formaldehyde formation is monitored via vibration–rotation lines of the  $\nu_2$  carbonyl stretch mode at 1729  $\text{cm}^{-1}$ . Radiation from a lead salt diode laser propagates through the cell and is focused onto a HgCdTe detector with a 0.3  $\mu\text{s}$  response time. The detector responds only to changes in IR light intensity; thus, the absolute intensity is added to the transient response prior to the use of Beer's law to extract the formaldehyde concentration via

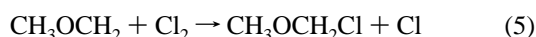
$$[\text{CH}_2\text{O}]_t = \frac{1}{\sigma_{\text{CH}_2\text{O}} l} \ln\left(\frac{I_0 + I(t)}{I_0}\right) \quad (3)$$

where  $l$  is the pathlength,  $\sigma_{\text{CH}_2\text{O}}$  is the IR absorption cross section, and  $I_0$  is the diode laser intensity. The absorption strength is measured at the temperature and pressure of each experiment and for each vibration–rotation line used as a probe by introducing a known amount of formaldehyde into the reaction cell. The formaldehyde is obtained by heating paraformaldehyde, and its concentration is confirmed by FT-IR analysis.

The oxidation and chain reaction studies of dimethyl ether were performed by combining laser flash photolysis to initiate the radical chemistry and the above described time-resolved spectroscopic techniques to monitor the important chemical species. Two sources of  $\text{CH}_3\text{OCH}_2$  were utilized: 351 nm photolysis of  $\text{Cl}_2$  followed by hydrogen abstraction from dimethyl ether,

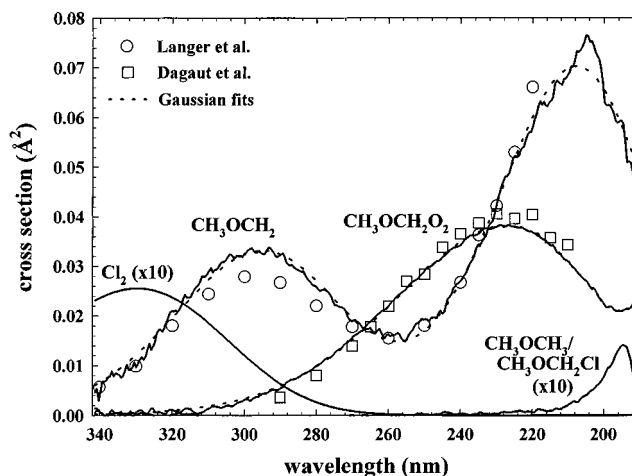


and 193 nm photolysis of phosgene into  $2\text{Cl} + \text{CO}$  followed by reaction 4. Because the rate constant for reaction 4 is large,<sup>6</sup>  $k_4 = 1.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , only a small amount of dimethyl ether (0.5 Torr) is required to convert the chlorine atoms produced by photolysis into methoxymethyl radicals on a short time scale (<0.5  $\mu\text{s}$ ) compared to the subsequent reactions of  $\text{CH}_3\text{OCH}_2$ . However, when  $\text{Cl}_2$  (~0.2 Torr) is used as the radical precursor, the situation is somewhat more complicated than for phosgene. The chain reaction



implies that a steady state population of chlorine atoms relative to  $\text{CH}_3\text{OCH}_2$ , equal to  $k_5[\text{Cl}_2]/k_4[\text{CH}_3\text{OCH}_3]$ , will be quickly established following chlorine photolysis. To ensure that this ratio is small, i.e., that the radical population consists predominantly of  $\text{CH}_3\text{OCH}_2$ , necessitates considerably higher dimethyl ether concentrations (~5 Torr).

A second difficulty incurred with the use of  $\text{Cl}_2$  photolysis to initiate the radical chemistry stems from our observation that



**Figure 1.** UV spectra of  $\text{CH}_3\text{OCH}_2$  and  $\text{CH}_3\text{OCH}_2\text{O}_2$ . These are compared to previously reported cross sections by Langer et al.<sup>9</sup> and Dagaut et al.,<sup>10</sup> respectively. The dotted traces represent the best fits of the spectra to a Gaussian line shape. Spectra of  $\text{Cl}_2$  and the  $\text{CH}_3\text{OCH}_3/\text{CH}_3\text{OCH}_2\text{Cl}$  composite are also illustrated for comparison.

dimethyl ether reacts spontaneously with molecular chlorine. To what extent this reaction is heterogeneous remains uncertain; however, the impact in our experiments was that only about 85% of the chlorine added to the reaction mixture actually reached the cell. This reaction is quenched by the addition of even a small amount of oxygen, implying that it likely proceeds via the intermediate  $\text{CH}_3\text{OCH}_2$  radical. Due to quenching by  $\text{O}_2$ , the spontaneous reaction affected only the measurements of the  $\text{CH}_3\text{OCH}_2 + \text{Cl}_2$  and  $\text{CH}_3\text{OCH}_2 + \text{CH}_3\text{OCH}_2$  reaction rate constants. The means of accounting for this interference is discussed in the Results section below.

The use of  $\text{COCl}_2$  as a chlorine atom source introduces two complications into the experiments. First, 193 nm light causes some  $\text{O}_2$  dissociation and the subsequent formation of ozone, a strong UV absorber. At the  $\text{O}_2$  concentrations employed in the present experiments, this problem occurred predominantly outside the cell, but within the photolysis and probe beam paths. The extent of ozone formation was measured independently and its contribution subtracted from the individual time-resolved spectra. Second, the 193 nm radiation dissociates some of the dimethyl ether reactant into  $\text{CH}_3$  and  $\text{CH}_3\text{O}$ . This is readily observed by the appearance of a sharp absorption feature at 216 nm characteristic of the methyl radical. Quantification of this absorption indicates that the formation of these dissociation products is limited to <15% of the Cl atom production under our experimental conditions. The effects of the methyl and methoxy radicals on our kinetics measurements are considered below.

The experiments were carried out using premixed gas mixtures, either  $\text{Cl}_2/\text{CH}_3\text{OCH}_3/\text{N}_2$  or  $\text{COCl}_2/\text{CH}_3\text{OCH}_3/\text{N}_2$ , each with or without added  $\text{O}_2$ , that are slowly flowed through a thermostated cylindrical cell that is 51 cm long and 3.2 cm in diameter. A 15 ns, 200–400 mJ, pulse from an excimer laser operating at 193 nm for  $\text{COCl}_2$ , or at 351 nm for  $\text{Cl}_2$ , passes longitudinally through the central portion of the cell (~1.5 cm diameter) of which the central 0.8 cm diameter region is probed. A Neslab ULT 80dd recirculating chiller maintains the cell temperature and preconditions the gas mixture over a range of 215–360 K. Tylan flow controllers are employed to regulate the individual gas flows, with the exception of  $\text{Cl}_2$ , which is adjusted by a needle valve.

## Results

**A. UV Spectra.** The UV spectrum of the  $\text{CH}_3\text{OCH}_2$  radical was measured in three ways: photolysis of phosgene in a

COCl<sub>2</sub>/CH<sub>3</sub>OCH<sub>3</sub>/N<sub>2</sub> gas mixture, photolysis of Cl<sub>2</sub> in a Cl<sub>2</sub>/CH<sub>3</sub>OCH<sub>3</sub>/N<sub>2</sub> mixture, and photolysis of Cl<sub>2</sub> in a Cl<sub>2</sub>/CH<sub>3</sub>OCH<sub>3</sub>/O<sub>2</sub>/N<sub>2</sub> mixture. The spectra were measured at a variety of times shortly after photolysis (2–10 μs) and extrapolated back to time zero. The initial concentration of chlorine atoms produced by the photolysis pulse was ascertained by substituting ethane for dimethyl ether, ensuring that oxygen was present in the gas mixture, and recording the absorption intensity of the ethylperoxy radicals that were formed.<sup>7</sup> Ethylperoxy radicals are rapidly formed, but only slowly removed via their self-reaction, and, thus, afford a convenient calibration standard.

The absorption intensities recorded from phosgene photolysis and from Cl<sub>2</sub> photolysis with oxygen present were in quantitative agreement over the 215–350 nm range. Information cannot be obtained below 215 nm for phosgene photolysis owing to the 193 nm optics used to introduce the photolysis beam into the cell. The absorption intensity measured using the Cl<sub>2</sub> precursor in the absence of oxygen was about 15% smaller than from the other two types of measurements, but otherwise exhibited the same wavelength dependence. Consistent with this observation, the 330 nm absorption of Cl<sub>2</sub> was found to fall by about 15% when dimethyl ether is introduced into the gas stream. As stated above, this occurs due to a (possibly heterogeneous) reaction between CH<sub>3</sub>OCH<sub>3</sub> and Cl<sub>2</sub> that depletes a small fraction of the chlorine prior to its reaching the cell.

The CH<sub>3</sub>OCH<sub>2</sub> spectrum determined from the three types of measurements is presented in Figure 1. It exhibits two absorption bands: one with a maximum at 295 nm and a second band having a maximum intensity at 204 nm. These two bands can be conveniently represented as the sum of two Gaussian profiles

$$\sigma(\lambda) = \sum_i \sigma_i \exp(-\alpha_i [\ln(\lambda_{i,\max}/\lambda)]^2) \quad (6)$$

with  $\sigma_1 = 7.0 \times 10^{-18} \text{ cm}^2$ ,  $a_1 = 47.8$ ,  $\lambda_{1,\max} = 208 \text{ nm}$ ,  $\sigma_2 = 3.3 \times 10^{-18} \text{ cm}^2$ ,  $a_2 = 81.4$ , and  $\lambda_{2,\max} = 295 \text{ nm}$ . As apparent from Figure 1, this expression gives a very good representation of the CH<sub>3</sub>OCH<sub>2</sub> spectrum, except for a small region near the peak of the short wavelength band, which the fitted expression underestimates by about 10%.

The CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> spectrum was measured by the same method as just described for the methoxymethyl radical, except that a high concentration of O<sub>2</sub>, ~10 Torr, was employed in the reaction mixture to convert rapidly the CH<sub>3</sub>OCH<sub>2</sub> radicals to peroxy radicals. The spectrum was measured as a function of O<sub>2</sub> pressure, total pressure, and time following photolysis. The O<sub>2</sub> and total pressures were increased until no change was noted upon further increase in either quantity; this occurs for [O<sub>2</sub>] > 5 Torr and P<sub>tot</sub> > 100 Torr. The latter condition is consistent with the observation that the CH<sub>3</sub>OCH<sub>2</sub> + O<sub>2</sub> reaction channel leading to formaldehyde represents less than about 5% of the overall reaction above this pressure.

The CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> spectra obtained from 193 nm photolysis of phosgene and 351 nm photolysis of Cl<sub>2</sub> are essentially identical. The spectrum, illustrated in Figure 1, is put on an absolute intensity scale by calibration against the absorption by ethylperoxy radicals. It consists of a broad absorption feature, as is typical of peroxy radicals, with the hint of a shorter wavelength band beginning below 200 nm. As evident from Figure 1, a Gaussian profile provides an excellent representation of the longer wavelength band of the CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> spectrum (for  $\lambda > 200 \text{ nm}$ ), being virtually indistinguishable from the experimental trace. In this case,  $\sigma = 3.8 \times 10^{-18} \text{ cm}^2$ ,  $a = 31.7$ , and  $\lambda_{\max} = 228 \text{ nm}$ .

**TABLE 1: Mechanism for the Cl<sub>2</sub>–CH<sub>3</sub>OCH<sub>3</sub> Chain Reaction**

reaction <sup>a</sup>	rate constant ( <i>k</i> )
4. Cl + CH <sub>3</sub> OCH <sub>3</sub> → CH <sub>3</sub> OCH <sub>2</sub> + HCl	1.9 × 10 <sup>-10</sup> cm <sup>3</sup> s <sup>-1</sup> <sup>6</sup>
5. CH <sub>3</sub> OCH <sub>2</sub> + Cl <sub>2</sub> → CH <sub>3</sub> OCH <sub>2</sub> Cl + Cl	1.8 × 10 <sup>-11</sup> e <sup>360/T</sup> cm <sup>3</sup> s <sup>-1</sup> <sup>b</sup>
7. CH <sub>3</sub> OCH <sub>2</sub> + CH <sub>3</sub> OCH <sub>2</sub> → (CH <sub>3</sub> OCH <sub>2</sub> ) <sub>2</sub>	1.8 × 10 <sup>-11</sup> e <sup>200/T</sup> cm <sup>3</sup> s <sup>-1</sup> <sup>b</sup>
8. CH <sub>3</sub> OCH <sub>2</sub> + Cl → products	(0–2) × 10 <sup>-10</sup> cm <sup>3</sup> s <sup>-1</sup>

When using 193 nm photolysis of COCl<sub>2</sub>, the reactions below were added to the model,<sup>c</sup> with the initial CH<sub>3</sub> and CH<sub>3</sub>O concentrations set equal to 15% of [Cl]<sub>0</sub>

CH <sub>3</sub> + CH <sub>3</sub> → C <sub>2</sub> H <sub>6</sub>	6 × 10 <sup>-11</sup> cm <sup>3</sup> s <sup>-1</sup>
CH <sub>3</sub> + CH <sub>3</sub> O → products	4 × 10 <sup>-11</sup> cm <sup>3</sup> s <sup>-1</sup>
CH <sub>3</sub> O + CH <sub>3</sub> O → products	3 × 10 <sup>-11</sup> cm <sup>3</sup> s <sup>-1</sup>
CH <sub>3</sub> OCH <sub>2</sub> + CH <sub>3</sub> → products	(0–6) × 10 <sup>-11</sup> cm <sup>3</sup> s <sup>-1</sup>
CH <sub>3</sub> OCH <sub>2</sub> + CH <sub>3</sub> O → products	(0–6) × 10 <sup>-11</sup> cm <sup>3</sup> s <sup>-1</sup>

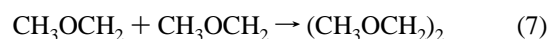
<sup>a</sup> Reaction numbers correspond to those used in the text. <sup>b</sup> Measured in the present study. <sup>c</sup> Rate constants are taken from the NIST database.<sup>8</sup> Those for the reactions involving CH<sub>3</sub>OCH<sub>2</sub> are varied over the indicated range.

The errors in the CH<sub>3</sub>OCH<sub>2</sub> and CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> absorption cross sections are estimated to be somewhat less than 10%. The ethylperoxy calibration spectrum is accurate to about 5%. An additional 5% is allowed for small changes that might have occurred when ethane and O<sub>2</sub> are substituted for dimethyl ether in the gas mixture and for the short extrapolation of the absorption to zero time.

The methoxymethyl and methoxymethylperoxy spectra discussed above are used to extract concentrations of the corresponding species from time-resolved spectra of the reaction mixture. The actual experimental spectra, and not the Gaussian fits, are used for this purpose. Besides these, two additional terms are included in the deconvolution represented by eq 2: the first accounts for the loss of molecular chlorine and the second is a composite term that accounts for the loss of dimethyl ether and the corresponding formation of CH<sub>3</sub>OCH<sub>2</sub>Cl. As previously stated, the latter two compounds absorb weakly in the region below about 210 nm, but with spectra that are not readily distinguishable. This term is included to preclude a systematic bias on the determination of the CH<sub>3</sub>OCH<sub>2</sub>, CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub>, and Cl<sub>2</sub> concentrations; however, its contribution to the overall absorption is not used in the subsequent kinetic analysis.

**B. Chain Reaction.** Photolysis of Cl<sub>2</sub> in the presence of CH<sub>3</sub>OCH<sub>3</sub> initiates a chain reaction represented by reactions 4 and 5. Figure 2 illustrates how the absorbance of the reaction mixture changes over time. At time zero, the two absorption bands characteristic of the methoxymethyl radical are evident. As time progresses, the intensities of these features decrease owing to the loss of this radical; however, the changes in intensity are not uniform over wavelength. At long times, a short wavelength feature appears at about 200 nm. Furthermore, the absorption decreases below zero in the 330 nm region.

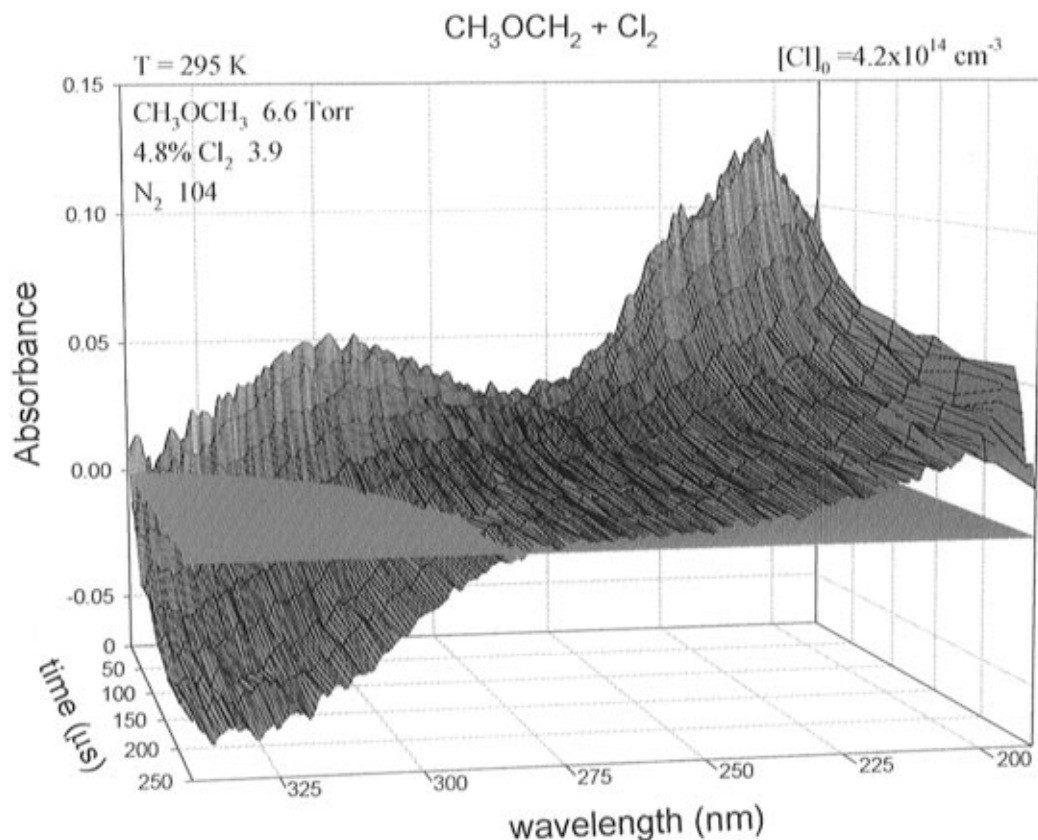
These spectral changes are consistent with a reaction mechanism (see Table 1) that consists of the chain propagation reactions as well as the termination reaction



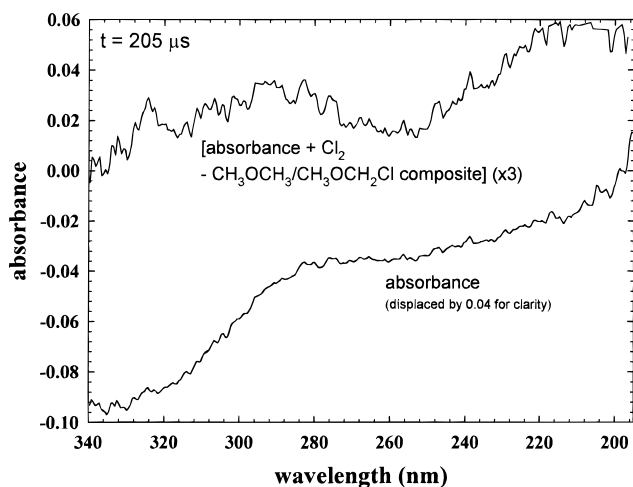
Reaction 7 accounts for the decreases in intensity of the bands at 295 and 204 nm. In principle, the reaction between methoxymethyl radicals and chlorine atoms,



also contributes, but under the present experimental conditions this reaction, as well as the chlorine atom recombination



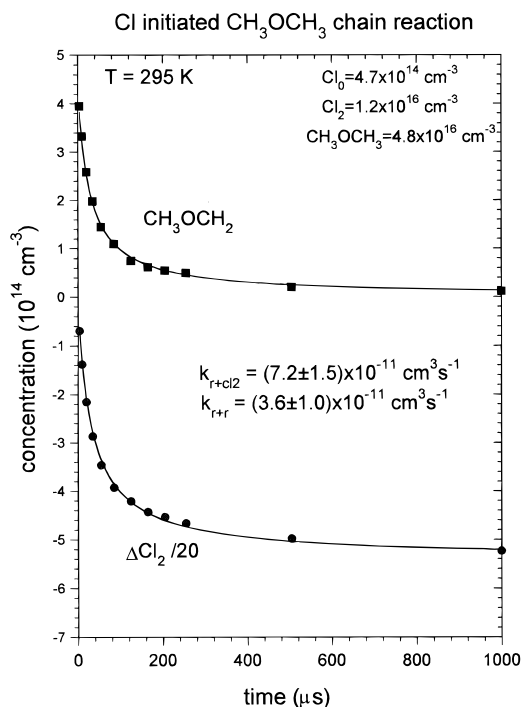
**Figure 2.** Absorbance–wavelength–time surface for the Cl-mediated chain reaction of dimethyl ether and chlorine.



**Figure 3.** Illustration of the deconvolution procedure for the 205  $\mu\text{s}$  time slice of Figure 2. Shown are the absorbance of the reaction mixture and the methoxymethyl contribution obtained after subtracting out the best fit contributions made by the  $\text{Cl}_2$  loss and the  $\text{CH}_3\text{OCH}_2/\text{CH}_3\text{OCH}_2\text{Cl}$  composite.

reaction, is unimportant since the steady state radical population fulfills  $[\text{CH}_3\text{OCH}_2]_{\text{ss}} \gg [\text{Cl}]_{\text{ss}}$ . Prior to its removal, however, each methoxymethyl radical cycles through reactions 4 and 5 roughly 20 times on average. This removes on the order of  $10^{16} \text{ cm}^{-3}$  chlorine molecules, explaining the negative absorbance that develops at 330 nm. The chain also converts an equal number of  $\text{CH}_3\text{OCH}_3$  molecules into  $\text{CH}_3\text{OCH}_2\text{Cl}$ . Each of these two species has an absorption band with an onset in the vicinity of 200 nm, but the chloride has the stronger absorption; thus the short wavelength feature appears at long times.

Fitting the time-resolved absorbances to reference spectra of  $\text{CH}_3\text{OCH}_2$ ,  $\text{Cl}_2$ , and the  $\text{CH}_3\text{OCH}_3/\text{CH}_3\text{OCH}_2\text{Cl}$  composite



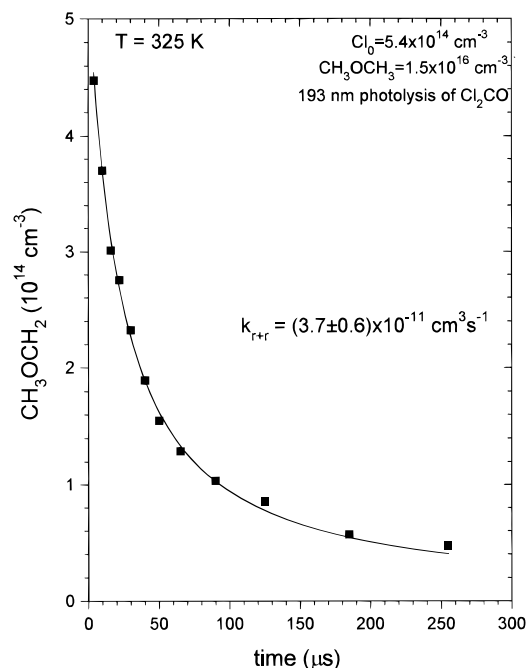
**Figure 4.** Methoxymethyl and molecular chlorine concentration versus time profiles obtained by deconvolution of the time-resolved spectra. The solid lines show best fits of the model in Table 1 to the data.

absorption provides time-varying concentration profiles for the methoxymethyl radical and chlorine. Figure 3 demonstrates the deconvolution procedure, and Figure 4 illustrates the resulting concentration profiles. The  $\text{Cl}_2$  concentrations have been scaled down by a factor of 20 for purposes of illustration and in order that they do not inordinately weight the fitting of the data to the reaction model.

**TABLE 2: Measured Rate Constants for the Reactions  $\text{CH}_3\text{OCH}_2 + \text{CH}_3\text{OCH}_2$  and  $\text{CH}_3\text{OCH}_2 + \text{Cl}_2$** 

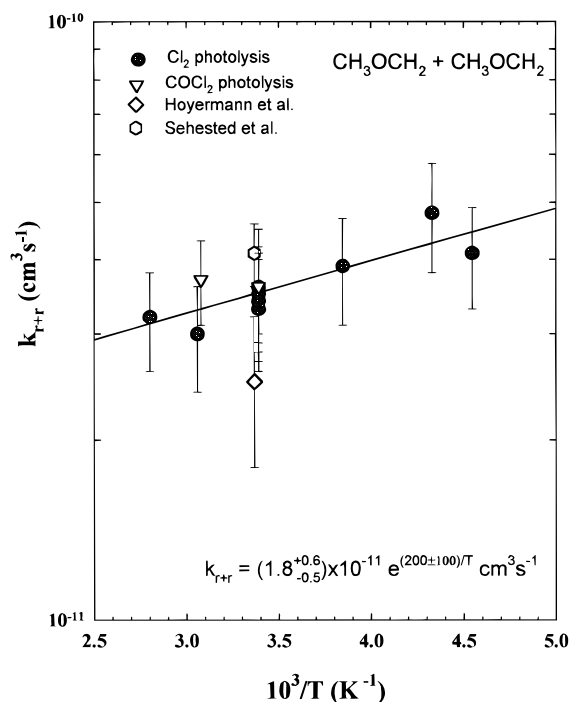
temp (K)	radical source <sup>a</sup> source; conc ( $10^{16} \text{ cm}^{-3}$ )	conditions			results <sup>b</sup>	
		$\text{CH}_3\text{OCH}_2$ ( $10^{16} \text{ cm}^{-3}$ )	$P_{\text{tot}}$ (Torr)	$[\text{Cl}]_0$ ( $10^{14} \text{ cm}^{-3}$ )	$k_{\text{r}+\text{r}}$ ( $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ )	$k_{\text{r}+\text{cl}_2}$ ( $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ )
220	$\text{Cl}_2$ ; 0.80	28	112	4.6	$4.1 \pm 0.8$	$9.3 \pm 1.5$
231	$\text{Cl}_2$ ; 1.2	27	413	5.3	$4.8 \pm 1.0$	$8.1 \pm 1.4$
260	$\text{Cl}_2$ ; 0.95	24	25	5.1	$3.9 \pm 0.8$	$7.0 \pm 1.3$
295	$\text{Cl}_2$ ; 0.64	5.0	112	3.6	$3.5 \pm 0.6$	$6.4 \pm 0.9$
295	$\text{Cl}_2$ ; 0.61	22	116	3.6	$3.3 \pm 0.7$	$6.4 \pm 1.0$
295	$\text{Cl}_2$ ; 0.85	21	114	6.8	$3.4 \pm 0.6$	$5.5 \pm 0.8$
295	$\text{Cl}_2$ ; 0.70	20	112	1.6	$3.4 \pm 0.7$	$6.2 \pm 0.8$
295	$\text{Cl}_2$ ; 1.2	4.8	113	4.6	$3.6 \pm 1.0$	$7.2 \pm 1.5$
295	$\text{COCl}_2$ ; 0.25	1.6	122	5.2	$3.6 \pm 0.6$	
325	$\text{COCl}_2$ ; 0.25	1.5	451	5.4	$3.7 \pm 0.6$	
327	$\text{Cl}_2$ ; 0.53	19	120	3.7	$3.0 \pm 0.6$	$5.0 \pm 0.9$
357	$\text{Cl}_2$ ; 0.86	17	58	4.4	$3.2 \pm 0.6$	$4.8 \pm 0.9$

<sup>a</sup> Listed concentrations are determined by measurements of gas flows. Due to the reaction between  $\text{Cl}_2$  and  $\text{CH}_3\text{OCH}_3$ , actual chlorine concentrations in the cell were approximately 85% of the tabulated value. <sup>b</sup> Error bars are  $\pm 2\sigma$  and include systematic uncertainties.



**Figure 5.** Decay of  $\text{CH}_3\text{OCH}_2$  produced by the photolysis of  $\text{COCl}_2$  in the presence of dimethyl ether. The solid line shows the fit of the data by the model.

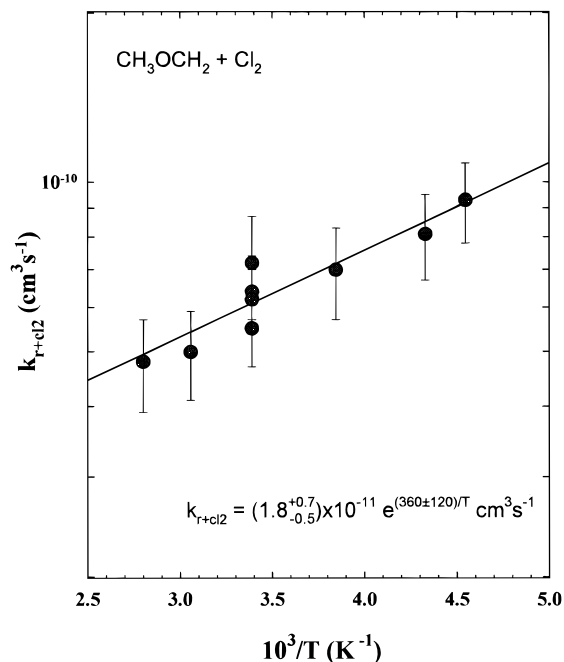
The concentration versus time data are fit to the reaction model of Table 1 treating  $k_{\text{r}+\text{r}}$  and  $k_{\text{r}+\text{cl}_2}$ , the rate constants for reactions 7 and 5, respectively, as adjustable parameters. Examples of the quality of fit are provided by the solid lines in Figure 4. The rate constants are collected, along with the pertinent experimental conditions, in Table 2. The errors are  $\pm 2\sigma$  and include both the data scatter and systematic uncertainties. In the case of  $k_{\text{r}+\text{cl}_2}$  the latter are dominated by uncertainties in the optical cross sections of  $\text{CH}_3\text{OCH}_2$  and  $\text{Cl}_2$  and in the initial radical concentration, as measured by the ethylperoxy calibration method. A 10% uncertainty in  $\sigma_{\text{ch}_3\text{o}ch_2}$  introduces a  $\sim 8\%$  error, a 5% uncertainty in  $\sigma_{\text{cl}_2}$  contributes 8%, and a 10% uncertainty in  $[\text{Cl}]_0$  contributes about 5% to the overall error in  $k_{\text{r}+\text{cl}_2}$ , whereas uncertainties in the values of  $k_4$  and  $k_8$  have a negligible impact. Combining these statistically with a 5% fitting error leads to  $2\sigma$  error bars in the vicinity of  $\pm 16\%$ . The errors in  $k_{\text{r}+\text{r}}$  also derive primarily from uncertainties in  $\sigma_{\text{ch}_3\text{o}ch_2}$ ,  $\sigma_{\text{cl}_2}$ , and  $[\text{Cl}]_0$ . In this case the fit is more sensitive to the  $\text{CH}_3\text{OCH}_2$  cross section, which contributes a 15% error, and the initial radical concentration, which contributes a 10% error. Combined with a 10% error from data scatter, the net error in  $k_{\text{r}+\text{r}}$  is approximately  $\pm 20\%$ .



**Figure 6.** Temperature dependence of the  $\text{CH}_3\text{OCH}_2$  self-reaction rate constant. Also shown are the values reported by Hoyermann et al.<sup>12</sup> and Sehested et al.<sup>11</sup>

Additional measurements of the  $\text{CH}_3\text{OCH}_2$  self-reaction rate constant were made using the photolysis of  $\text{COCl}_2$  in the presence of dimethyl ether. After removing the contribution made by ozone formed outside the reaction cell, the time-resolved spectra reveal the characteristic methoxymethyl absorption bands, which decay in time without changes in the wavelength dependence. This is consistent with the second-order removal of  $\text{CH}_3\text{OCH}_2$  into a form having at most a minor optical absorption in the 200–340 nm range. The time dependence of  $[\text{CH}_3\text{OCH}_2]$  at 325 K derived from these spectra is provided by Figure 5.

The analysis of the data when using the  $\text{COCl}_2$  precursor differs somewhat from the above discussion. In the absence of  $\text{Cl}_2$  the chain reaction plays no role; thus, reaction 5 is omitted from the model. However, additional chemistry, listed in Table 1, is included to account for reactions of the  $\text{CH}_3$  and  $\text{CH}_3\text{O}$  radicals that are produced from the 193 nm photolysis of  $\text{CH}_3\text{OCH}_3$  (kinetic data for these reactions are obtained from the NIST database<sup>8</sup>). Their rates of reaction with  $\text{CH}_3\text{OCH}_2$  are unknown and, thus, introduce an uncertainty into the determi-



**Figure 7.** Temperature dependence of the  $\text{CH}_3\text{OCH}_2 + \text{Cl}_2$  reaction rate constant.

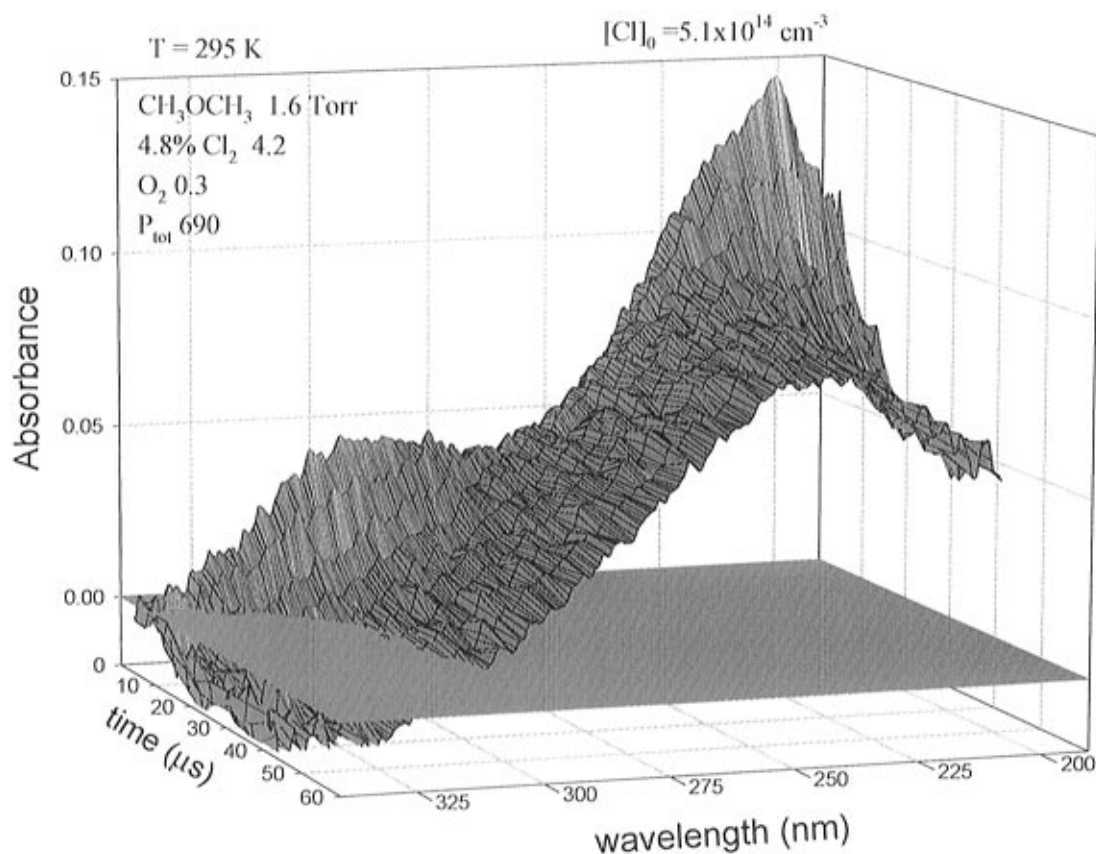
nation of  $k_{r+r}$ . Fortunately this uncertainty is small since the initial  $\text{CH}_3$  and  $\text{CH}_3\text{O}$  concentrations are approximately 8 times less than  $[\text{Cl}]_0$ . Thus, variation of the rate constants over the range  $(0-6) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , a range reasonable for radical-radical reactions between alkyl and alkoxy radicals, affects the best fit values of  $k_{r+r}$  by about  $\pm 7\%$ . The rate constants derived from this modified model, listed in Table 1, are in excellent agreement with those derived from  $\text{Cl}_2$  photolysis. In addition to the uncertainties introduced by dimethyl ether dissociation,

there are 10% errors from data scatter and from the uncertainty in  $\sigma_{\text{ch}_3\text{o}_2}$  that result in a statistically combined  $2\sigma$  error of  $\sim \pm 17\%$ .

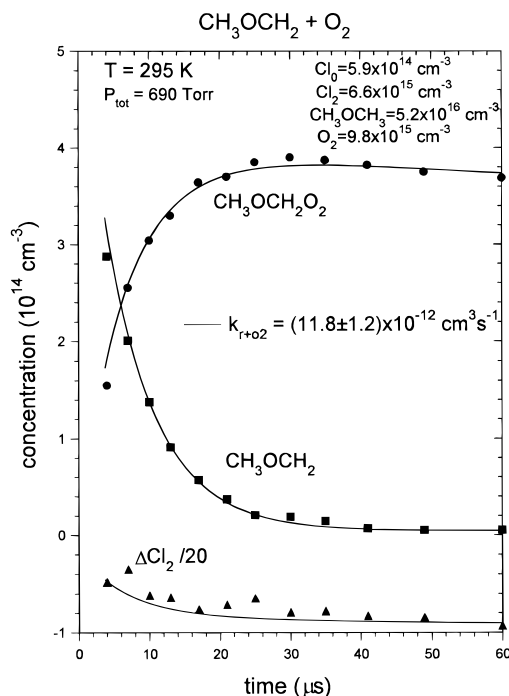
The variations with temperature of the rate constants for the  $\text{CH}_3\text{OCH}_2$  self-reaction and its reaction with chlorine are presented in Figures 6 and 7, respectively. Both exhibit a negative temperature dependence, which is mildly surprising in the case of the radical-molecule reaction. Expressed in the Arrhenius form, the self reaction rate constant is given by  $k_{r+r} = (1.8^{+0.6}_{-0.5}) \times 10^{-11} e^{(200 \pm 100)/T} \text{ cm}^3 \text{ s}^{-1}$ , whereas the rate constant for the reaction with molecular chlorine is  $k_{r+\text{cl}_2} = (1.8^{+0.7}_{-0.5}) \times 10^{-11} e^{(360 \pm 120)/T} \text{ cm}^3 \text{ s}^{-1}$ .

**C. Reaction of  $\text{CH}_3\text{OCH}_2$  with  $\text{O}_2$ .** *i. High Pressure: The Peroxy Radical Channel.* Adding oxygen to a  $\text{Cl}_2/\text{CH}_3\text{OCH}_2/\text{N}_2$  gas mixture dramatically changes the shape of the absorption-wavelength-time surface recorded following  $\text{Cl}_2$  photolysis, as is evident from comparing Figures 8 and 2. In both cases, the absorption at early time is characteristic of the methoxymethyl radical; however, the decay below zero of the absorption at 330 nm is less pronounced when oxygen is present, and more importantly, a new absorption feature peaking at about 225 nm appears rapidly, within 50  $\mu\text{s}$  of the photolysis pulse. This new feature matches the  $\text{CH}_3\text{OCH}_2\text{O}_2$  spectrum illustrated in Figure 1.

Qualitatively these changes in the optical absorption of the reaction mixture are what one would expect from the addition of  $\text{O}_2$  to the methoxymethyl radical to yield the corresponding peroxy radical. Fits of the time-resolved spectra to reference spectra of  $\text{CH}_3\text{OCH}_2$ ,  $\text{CH}_3\text{OCH}_2\text{O}_2$ ,  $\text{Cl}_2$ , and the  $\text{CH}_3\text{OCH}_2/\text{CH}_3\text{OCH}_2\text{Cl}$  composite yield the concentration versus time profiles illustrated in Figure 9. The decay of the methoxymethyl radical is accompanied by a rapid rise in  $\text{CH}_3\text{OCH}_2\text{O}_2$  concentration. There is still some loss of  $\text{Cl}_2$ ; however, it is diminished when oxygen is present because the  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  reaction



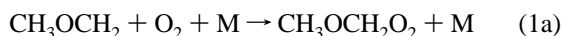
**Figure 8.** Absorbance-wavelength-time surface for the  $\text{Cl}$ -initiated oxidation of dimethyl ether.



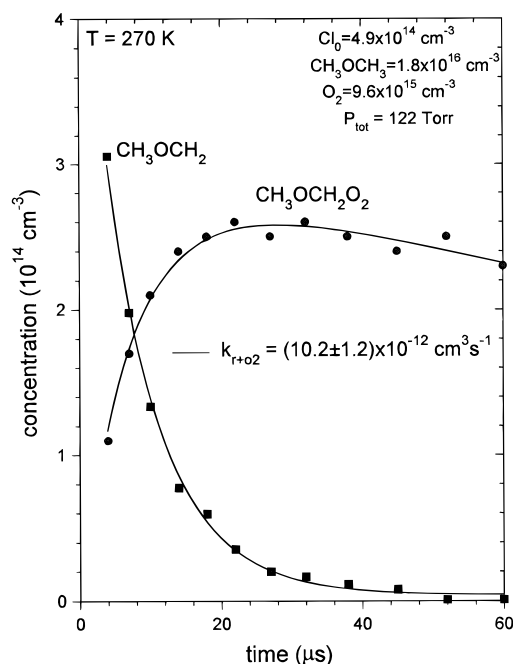
**Figure 9.** Methoxymethyl, methoxymethylperoxy, and molecular chlorine concentration versus time profiles obtained by deconvolution of time-resolved spectra obtained using  $\text{Cl}_2$  photolysis. The solid lines show best fits of the model in Table 3 to the data.

acts as an additional chain termination step. The results remain unchanged when the  $\text{CH}_3\text{OCH}_2$  radical is generated by  $\text{COCl}_2$  photolysis, as shown by Figure 10, except for the obvious fact that there is no accompanying  $\text{Cl}_2$  loss.

The apparent simplicity of the above discussion belies a number of underlying complexities inherent in this system. The principal one, the pressure dependence of the  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  reaction, is discussed below; here we consider the mechanism assuming that only the peroxy radical is formed, which is appropriate for total pressures greater than about 100 Torr.<sup>3</sup> Even under these conditions, however, simply augmenting the chain reaction of Table 1 with the reaction

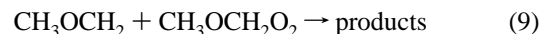


is not sufficient to permit satisfactory fits of the data; the model



**Figure 10.** Methoxymethyl and methoxymethylperoxy concentration versus time profiles obtained by deconvolution of time-resolved spectra obtained using phosgene photolysis. The solid lines show best fits of the model in Table 3 to the data.

underestimates the rate of methoxymethyl radical decay and overestimates the quantity of peroxy radicals formed. Adding the cross reaction



corrects these deficiencies and leads to excellent fits of the data, treating  $k_{r+o2}$  and  $k_9$  as adjustable parameters. The values obtained for  $k_9$  lie in the range  $(2-8) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ; those for  $k_{r+o2}$  are listed in Table 3.

The fits of the concentration versus time profiles shown by the solid lines in Figures 9 and 10 are obtained using the more complete reaction mechanism provided in Table 4 (including a contribution by channel 1b of <6% at  $P_{\text{tot}} > 100$  Torr), although the additional chemistry only slightly affects the fits. Aside from the above reactions this model includes the peroxy radical self-reaction and the ensuing regeneration

**TABLE 3: Measured Rate Constants for the  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  Reaction**

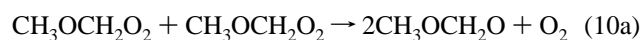
temp (K)	radical source source; conc ( $10^{16} \text{ cm}^{-3}$ )	conditions				results $k_{r+o2}$ ( $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ )
		$\text{CH}_3\text{OCH}_3$ ( $10^{16} \text{ cm}^{-3}$ )	$\text{O}_2$ ( $10^{16} \text{ cm}^{-3}$ )	$P_{\text{tot}}$ (Torr)	$[\text{Cl}]_0$ ( $10^{14} \text{ cm}^{-3}$ )	
versus $T$ at $\sim 120$ Torr						
220	$\text{Cl}_2$ ; 0.82	26	1.0	111	4.6	$12.9 \pm 1.7$
229	$\text{COCl}_2$ ; 1.1	2.1	1.1	118	5.3	$12.4 \pm 2.0$
252	$\text{Cl}_2$ ; 0.77	8.8	0.77	108	4.9	$13.1 \pm 1.8$
270	$\text{COCl}_2$ ; 0.89	1.8	0.96	120	4.9	$10.2 \pm 1.2$
295	$\text{COCl}_2$ ; 0.84	1.6	0.47	119	5.6	$9.3 \pm 1.4$
295	$\text{Cl}_2$ ; 0.64	4.8	0.78	110	4.4	$9.2 \pm 1.2$
295	$\text{COCl}_2$ ; 0.86	1.6	0.89	122	5.7	$9.5 \pm 1.1$
295	$\text{COCl}_2$ ; 0.84	1.6	1.8	122	5.4	$9.4 \pm 1.2$
295	$\text{COCl}_2$ ; 1.7	1.6	1.7	125	6.0	$8.9 \pm 1.2$
355	$\text{Cl}_2$ ; 0.59	6.4	0.6	110	3.7	$7.6 \pm 1.0$
versus $P_{\text{tot}}$ at 295 K						
295	$\text{Cl}_2$ ; 0.58	5.2	0.49	5.4	3.2	$8.5 \pm 1.5$
295	$\text{Cl}_2$ ; 0.71	5.2	1.4	6.5	5.6	$7.1 \pm 1.2$
295	$\text{COCl}_2$ ; 0.87	1.6	0.87	53	5.2	$9.0 \pm 1.1$
295	$\text{COCl}_2$ ; 0.86	1.5	0.85	206	5.0	$10.0 \pm 1.3$
295	$\text{COCl}_2$ ; 0.89	1.6	0.81	442	5.6	$10.8 \pm 1.3$
295	$\text{Cl}_2$ ; 0.70	8.0	0.75	480	4.4	$11.6 \pm 1.8$
295	$\text{Cl}_2$ ; 0.70	5.2	0.98	690	5.9	$11.8 \pm 1.2$

**TABLE 4: Mechanism for the CH<sub>3</sub>OCH<sub>2</sub> + O<sub>2</sub> Reaction**

reaction <sup>a</sup>	Principal	rate constant ( <i>k</i> )
4. Cl + CH <sub>3</sub> OCH <sub>3</sub> → CH <sub>3</sub> OCH <sub>2</sub> + HCl	Principal	1.9 × 10 <sup>-10</sup> cm <sup>3</sup> s <sup>-1</sup> <sup>6</sup>
1a. CH <sub>3</sub> OCH <sub>2</sub> + O <sub>2</sub> + M → CH <sub>3</sub> OCH <sub>2</sub> O <sub>2</sub> + M		see text
1b. CH <sub>3</sub> OCH <sub>2</sub> + O <sub>2</sub> → 2CH <sub>2</sub> O + OH		see text
	Radical–Radical	
10a. CH <sub>3</sub> OCH <sub>2</sub> O <sub>2</sub> + CH <sub>3</sub> OCH <sub>2</sub> O <sub>2</sub> → 2CH <sub>3</sub> OCH <sub>2</sub> O + O <sub>2</sub>		(3–6) × 10 <sup>-12</sup> cm <sup>3</sup> s <sup>-1</sup>
10b. CH <sub>3</sub> OCH <sub>2</sub> O <sub>2</sub> + CH <sub>3</sub> OCH <sub>2</sub> O <sub>2</sub> → CH <sub>3</sub> OCHO + CH <sub>3</sub> OCH <sub>2</sub> OH + O <sub>2</sub>		(1–2) × 10 <sup>-12</sup> cm <sup>3</sup> s <sup>-1</sup>
7. CH <sub>3</sub> OCH <sub>2</sub> + CH <sub>3</sub> OCH <sub>2</sub> → (CH <sub>3</sub> OCH <sub>2</sub> ) <sub>2</sub>		1.8 × 10 <sup>-11</sup> e <sup>200/T</sup> cm <sup>3</sup> s <sup>-1</sup> <sup>b</sup>
9. CH <sub>3</sub> OCH <sub>2</sub> + CH <sub>3</sub> OCH <sub>2</sub> O <sub>2</sub> → products		(2–8) × 10 <sup>-11</sup> cm <sup>3</sup> s <sup>-1</sup>
8. CH <sub>3</sub> OCH <sub>2</sub> + Cl → products		(0–2) × 10 <sup>-10</sup> cm <sup>3</sup> s <sup>-1</sup>
	Chain	
13. OH + CH <sub>3</sub> OCH <sub>3</sub> → CH <sub>3</sub> OCH <sub>2</sub> + H <sub>2</sub> O		6.7 × 10 <sup>-12</sup> e <sup>-300/T</sup> cm <sup>3</sup> s <sup>-1</sup> <sup>8</sup>
11. CH <sub>3</sub> OCH <sub>2</sub> O → CH <sub>3</sub> OCHO + H		0–∞ s <sup>-1</sup>
12. H + CH <sub>3</sub> OCH <sub>2</sub> O <sub>2</sub> → CH <sub>3</sub> OCH <sub>2</sub> O + OH		(0–1) × 10 <sup>-10</sup> cm <sup>3</sup> s <sup>-1</sup>
H + Cl <sub>2</sub> → Cl + HCl		1.4 × 10 <sup>-10</sup> e <sup>-590/T</sup> cm <sup>3</sup> s <sup>-1</sup> <sup>8</sup>
5. CH <sub>3</sub> OCH <sub>2</sub> + Cl <sub>2</sub> → CH <sub>3</sub> OCH <sub>2</sub> Cl + Cl		1.8 × 10 <sup>-11</sup> e <sup>360/T</sup> cm <sup>3</sup> s <sup>-1</sup> <sup>b</sup>

<sup>a</sup> Reaction numbers correspond to those used in the text. <sup>b</sup> Measured in the present study.

of CH<sub>3</sub>OCH<sub>2</sub> radicals. The latter occurs via



in which one channel of the CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> peroxy radical self-reaction yields the corresponding alkoxy radical, which subsequently ejects a hydrogen atom. The competing reaction between CH<sub>3</sub>OCH<sub>2</sub>O and O<sub>2</sub> is too slow at the oxygen concentrations of this study to be of consequence. Hydrogen atoms formed by reaction 11 can add O<sub>2</sub>, which is slow under the present conditions because of the low O<sub>2</sub> concentrations employed, react with dimethyl ether, which is slow compared to the Cl<sub>2</sub> reaction, or react with Cl<sub>2</sub> to regenerate chlorine atoms. Potentially they could also react with peroxy radicals,



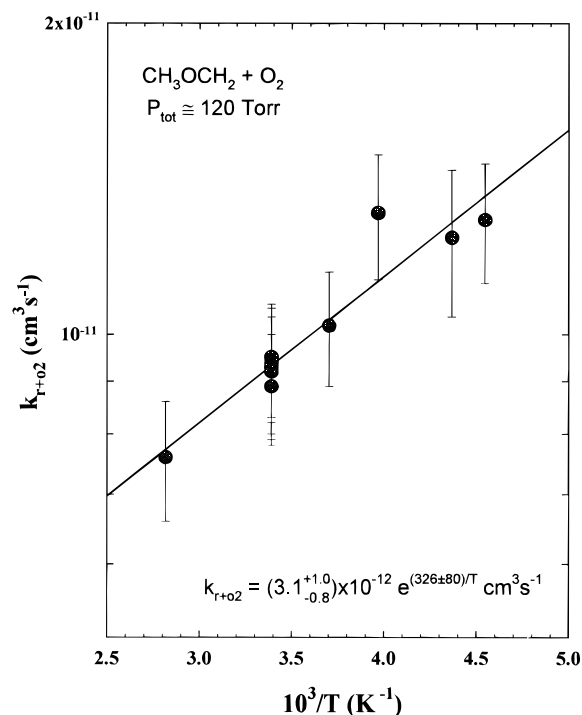
with the interesting consequence of producing one methoxy-methyl radical, from OH attack of dimethyl ether, and regenerating the hydrogen atom via reaction 11. Although provided here for completeness and although important for understanding the subsequent chemistry of the CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> radicals, reactions 10–12 have only a minor influence on the decay of the methoxymethyl radical and on the determination of *k*<sub>r+o2</sub>.

The temperature dependence of the CH<sub>3</sub>OCH<sub>2</sub> + O<sub>2</sub> reaction was investigated at a total pressure in the vicinity of 120 Torr. The results are listed in Table 3 and illustrated by Figure 11. A fit of the data to the Arrhenius form yields *k*<sub>r+o2</sub>(120 Torr) = (3.1<sup>+1.0</sup><sub>-0.8</sub>) × 10<sup>-12</sup>e<sup>(326±80)/T</sup> cm<sup>3</sup> s<sup>-1</sup>. The reaction exhibits a negative temperature dependence, as expected for an addition reaction.

*ii. Low Pressure: The Hydroxyl Radical Channel.* The data shown in Figures 8–11 and described above were recorded at pressures greater than 100 Torr. Another level of complexity arises as the total pressure is lowered below this level. The product study of Sehested et al.<sup>3</sup> observed an increase in formaldehyde formation, from about 15% at 100 Torr to 120% at 5 Torr, which they attributed to the competing reaction channel

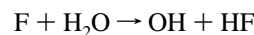


A direct observation of this channel is presented in Figure 12, which shows the absorbance of a Cl<sub>2</sub>/CH<sub>3</sub>OCH<sub>3</sub>/O<sub>2</sub> gas mixture at 5.5 Torr total pressure 8 μs after photolysis. The upper trace reveals the *v*' = 0 → *v*' = 0 and *v*' = 0 → *v*' = 1 bands of the



**Figure 11.** Temperature dependence of the reaction between CH<sub>3</sub>OCH<sub>2</sub> and O<sub>2</sub> at 120 Torr total pressure.

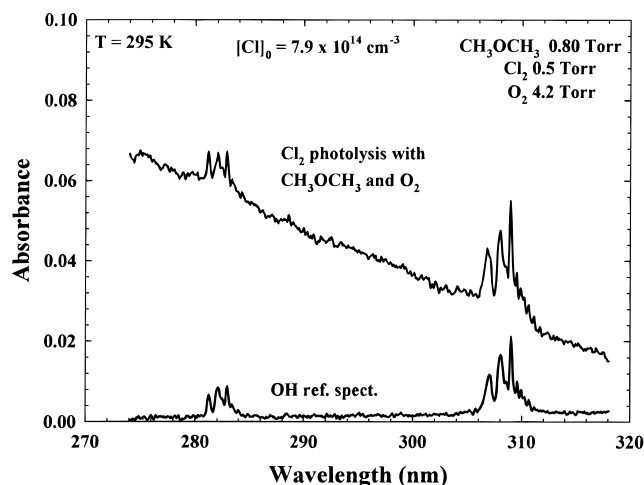
X <sup>2</sup>Π → A <sup>2</sup>Σ<sup>+</sup> transition of the hydroxyl radical at 308.6 and 282.5 nm, respectively, which are superimposed on the long wavelength tail of the CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub> spectrum. This is confirmed by the OH spectrum shown in the lower trace, which is obtained by the photolysis of F<sub>2</sub> in the presence of water vapor via the reaction



By calibrating the OH absorption intensity at the spectral resolution of our spectrometer against the absorption by ethylperoxy radicals formed when ethane and O<sub>2</sub> are substituted for water vapor, we find the OH concentration in the upper trace to be 2.8 × 10<sup>14</sup> cm<sup>-3</sup>, a value in good agreement with the reaction mechanism given in Table 4 and discussed below.

Direct observation of channel 1b is also provided by the IR diode laser transient absorption measurements of formaldehyde generation that are presented in Figure 13. The amount of CH<sub>2</sub>O formed falls with increasing total pressure such that the branching fraction for channel 1b decreases from *f* = 0.45 at





**Figure 12.**  $X^2\Pi \rightarrow A^2\Sigma^+$  transition of the hydroxyl radical formed from the reaction between  $\text{CH}_3\text{OCH}_2$  and  $\text{O}_2$ .

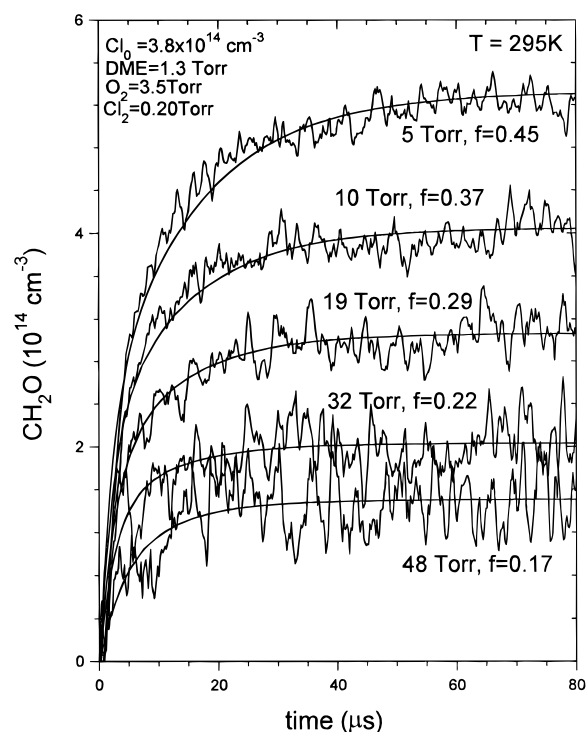
$P_{\text{tot}} = 5$  Torr to a value of 0.17 at 48 Torr. Similar results are obtained when phosgene, as opposed to chlorine, photolysis is used to initiate the reaction (see Table 5).

Aside from the fact that two competing channels are active below about 100 Torr, the formation of OH further complicates matters. It introduces an additional chain reaction into the overall mechanism since the hydroxyl radical will attack dimethyl ether,



and regenerate a methoxymethyl radical. This is included in the reaction mechanism of Table 4. Fitting the formaldehyde formation traces to this model, treating  $k_{r+o2}$  and  $f$  as adjustable parameters and setting  $k_9 = 5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , leads to the smooth line fits of the data shown in Figure 13.

As seen from Table 5, the values of  $k_{r+o2}$  obtained from these fits are in the range  $(2.8\text{--}5.5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , 2–3 times smaller than the rate constant at  $P_{\text{tot}} > 100$  Torr. In fact, the rate constants found from formaldehyde formation are smaller by roughly a factor of 2 than those determined at the same total pressure from  $\text{CH}_3\text{OCH}_2$  loss and  $\text{CH}_3\text{OCH}_2\text{O}_2$  formation using time-resolved UV spectroscopy. A plausible explanation for



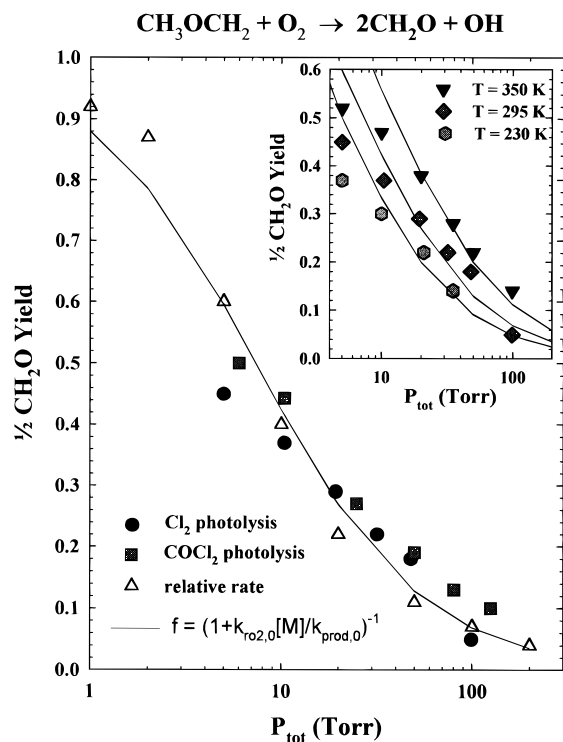
**Figure 13.** IR diode laser transient absorption measurements of the formaldehyde formed from the  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  reaction as a function of total pressure.

this is as follows. The formation of formaldehyde and the hydroxyl radical via reaction 1b is exothermic by 40 kcal/mol. This excess energy is sufficient to produce vibrationally excited  $\text{CH}_2\text{O}$  molecules. Since the diode laser probes the  $\nu = 0 \rightarrow \nu = 1$  transition of the  $\nu_2$  carbonyl stretch, excited molecules would initially be transparent to the probe. As time progresses and the excited molecules are collisionally relaxed to the ground state, they would contribute to the total IR absorbance. Consequently, the observed rate constant for  $\text{CH}_2\text{O}$  formation, being a convolution of  $f k_{r+o2}$  and the vibrational relaxation rate constant, will appear smaller than the true value. This problem should decrease as  $P_{\text{tot}}$  increases owing to faster relaxation; however, sensitivity also decreases because of line broadening

**TABLE 5: Yield of Channel 1b from Transient  $\text{CH}_2\text{O}$  Measurements**

temp (K)	radical source source; conc ( $10^{16} \text{ cm}^{-3}$ )	conditions				results <sup>a</sup>		
		$\text{CH}_3\text{OCH}_3$ ( $10^{16} \text{ cm}^{-3}$ )	$\text{O}_2$ ( $10^{16} \text{ cm}^{-3}$ )	$P_{\text{tot}}$ (Torr)	$[\text{Cl}]_0$ ( $10^{14} \text{ cm}^{-3}$ )	$k_{r+o2}$ ( $10^{-12} \text{ cm}^3 \text{ s}^{-1}$ )	$f$	
230	$\text{Cl}_2$ ; 0.80	5.5	14	4.9	4.9	4.7	0.37	
230	$\text{Cl}_2$ ; 0.80	5.5	14	10.0	4.5	3.6	0.30	
230	$\text{Cl}_2$ ; 0.84	5.5	15	21.0	4.7	2.5	0.22	
230	$\text{Cl}_2$ ; 0.84	5.5	14	34.7	4.9		0.14	
295	$\text{Cl}_2$ ; 0.65	4.3	11	4.9	3.5	3.7	0.46	
295	$\text{Cl}_2$ ; 0.65	4.3	12	10.2	3.8	3.5	0.37	
295	$\text{Cl}_2$ ; 0.65	4.3	11	19.0	4.0	3.1	0.29	
295	$\text{Cl}_2$ ; 0.65	4.3	11	32.0	3.8	3.4	0.22	
295	$\text{Cl}_2$ ; 0.65	4.3	11	47.5	3.9		0.18	
295	$\text{COCl}_2$ ; 1.0	4.3	13	6	4.1	2.8	0.50	
295	$\text{COCl}_2$ ; 0.85	4.3	11	10.4	4.1	3.0	0.44	
295	$\text{COCl}_2$ ; 0.82	4.3	11	24.9	4.6	2.5	0.27	
295	$\text{COCl}_2$ ; 0.82	4.3	11	50.1	5.0	1.2	0.19	
295	$\text{COCl}_2$ ; 0.88	4.3	12	80.3	5.1		0.13	
350	$\text{Cl}_2$ ; 0.55	3.6	9.4	5	3.2	3.4	0.52	
350	$\text{Cl}_2$ ; 0.55	3.6	9.2	10	2.9	3.0	0.47	
350	$\text{Cl}_2$ ; 0.52	3.6	8.8	20	3.7	3.0	0.38	
350	$\text{Cl}_2$ ; 0.58	3.6	9.9	35	3.8	2.5	0.28	
350	$\text{Cl}_2$ ; 0.58	3.6	9.7	50	3.2	3.3	0.22	

<sup>a</sup> The values of  $k_{r+o2}$  and  $f$  are lower bounds owing to possible vibrational excitation of the  $\text{CH}_2\text{O}$ ; see text.  $f$  is the branching fraction for reaction 1b.



**Figure 14.** Pressure dependence of the branching fraction for the formaldehyde channel of the  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  reaction. Also shown are values from the product study of Sehested et al.<sup>3</sup> The inset shows the variation with temperature of the pressure dependent formaldehyde channel.

whereby the measurement of  $k_{r+o2}$  becomes less reliable. An example of the extent to which nascent vibrational excitation can mask the true kinetics is provided in a previous paper<sup>5</sup> investigating ethylene formation from the reaction of  $\text{C}_2\text{H}_5$  and  $\text{Cl}$ .

By similar arguments, generation of excited formaldehyde by reaction 1b will lead to underestimates of the branching fraction for this channel that depend systematically on the total pressure. Rigorously then, the pressure dependent formaldehyde yields exhibited in Figure 14 and listed in Table 5 would be expected to represent lower limits of the yield. However, as comparison to the product study of Sehested et al.<sup>3</sup> reveals, the limit is quite close to the actual values. This is likely because the branching fraction, which is determined by the level of formaldehyde at relatively long times (80  $\mu\text{s}$  in Figure 13), is less sensitive to vibrational relaxation than  $k_{r+o2}$ , which depends predominantly on the shape of the formaldehyde curve at short times (0–20  $\mu\text{s}$ ). Close examination of Figure 14 reveals that vibrational excitation may have some effect on the determination of  $f$ ; the  $\text{CH}_2\text{O}$  yield as recorded by transient IR absorption is somewhat smaller than that determined via the product study at the lowest pressure. The inset to Figure 14 compares the pressure dependence of the  $\text{CH}_2\text{O}$  yield at various temperatures. Increasing the temperature at a set total pressure has the effect of promoting formaldehyde formation, channel 1b, relative to peroxy radical formation, channel 1a.

*iii. Error Analysis.* The quantities of interest in the investigation of the  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  reaction kinetics are  $k_{r+o2}$  and  $f = k_{1b}/k_{r+o2}$  (where  $k_{r+o2} \equiv k_{1a} + k_{1b}$ ), the branching fraction for the formaldehyde channel. For measurements conducted using time-resolved UV absorption, the data were fit to the reaction model of Table 4, with  $k_{r+o2}$ ,  $k_9$ , and  $k_{10}$  treated as adjustable parameters. In these cases, the branching fraction was fixed to the value reported in ref 3, because, as discussed above, the present IR measurements of  $f$  could underestimate it

due to vibrational excitation of the nascent  $\text{CH}_2\text{O}$ . The transient IR measurements of formaldehyde were fit to the same model, except that  $k_{r+o2}$  and  $f$  were allowed to vary, whereas  $k_9$  and  $k_{10}$  were fixed to the midpoints of their respective ranges, as determined from the fits of the UV data.

For the UV measurements made with  $P_{\text{tot}} > 100$  Torr, the errors in  $k_{r+o2}$  arise predominantly from the fitting error and uncertainties in  $\sigma_{\text{ch}_3\text{oach}_2}$ ,  $\sigma_{\text{ch}_3\text{oach}_2\text{o}_2}$ , and  $f$ . The fitting error amounts to about 8% and includes contributions from data scatter and the uncertainty in  $k_9$  (as stated previously,  $k_{10}$  has little influence on  $k_{r+o2}$ ; it affects the decay of  $\text{RO}_2$ ). Uncertainties of 10% in the absolute intensities of the reference UV spectra each contribute roughly 7% to the overall error. Variation of  $f$  between 0 and 0.1, nearly twice the measured value at 100 Torr, introduces another 5% error into  $k_{r+o2}$ . Smaller contributions come from uncertainties of 10% in  $[\text{Cl}]_0$ , 20% in  $k_{r+o2}$ , and 10% in  $k_4$ , which introduce errors of 4%, 1.5%, and 2%, respectively. Combining these errors statistically yields a typical error in  $k_{r+o2}$  of  $\pm 15\%$ .

The preceding error analysis applies to results obtained using both  $\text{Cl}_2$  and  $\text{COCl}_2$  photolysis. Recall that, with respect to  $k_{r+o2}$  and  $k_{r+o2}$ , an additional error arises when phosgene is the precursor from the uncertainties introduced by small quantities of  $\text{CH}_3$  and  $\text{CH}_3\text{O}$  radicals produced by the 193 nm photolysis of dimethyl ether. The interference by these radicals in the measurement of  $k_{r+o2}$  is much smaller, because the loss of the  $\text{CH}_3\text{OCH}_2$  radical is dominated by its reaction with  $\text{O}_2$ . Instead, their impact will be on the subsequent chemistry of the  $\text{RO}_2$  radical.

Errors in the UV measurements of  $k_{r+o2}$  for  $P_{\text{tot}} < 100$  Torr become progressively larger as the total pressure decreases. Mainly this due to the more complex chemistry inherent at low pressure; partly it is due to loss in signal to noise owing to the reduced levels of peroxy radicals that are formed. By 5 Torr the net error is close to  $\pm 20\%$ . In principle the reverse is true for the IR measurements based on formaldehyde formation. Owing to collisional line broadening, the sensitivity of the technique increases as  $P_{\text{tot}}$  decreases. Unfortunately, vibrational relaxation rates decrease as the pressure is lowered; thus, the increase in sensitivity is offset by the increasing influence of the relaxation process on the rate of formaldehyde appearance. The determinations of  $f$  suffer the same fate, but to a lesser extent. The best estimate of their accuracy is probably obtained by comparison of our results to those obtained from the product study of Sehested et al.<sup>3</sup>

## Discussion

**A. UV Spectra.** The UV spectrum of the methoxymethyl radical is compared in Figure 1 to previous work by Langer et al.<sup>9</sup> In extrapolating to zero time, small corrections ( $\sim 10\%$ ) have been made to the spectrum to account for  $\text{CH}_3\text{OCH}_2$  loss,  $\text{Cl}_2$  loss,  $\text{CH}_3\text{OCH}_3$  loss, and  $\text{CH}_3\text{OCH}_2\text{Cl}$  formation. As evident from the figure, there is good agreement between the general features of the two spectra. Both reveal two absorption bands and agree on the wavelength maximum of the longer wavelength band. There is a small discrepancy between the two spectra in that the intensity of the 295 nm band recorded by Langer et al.<sup>9</sup> is roughly 15% smaller than the present measurement, whereas the intensities of the short wavelength bands appear to be in good agreement. This could be due to systematic variability incurred in making single-point intensity measurements that are absent in the present experiments in which the entire spectrum is measured simultaneously.

The  $\text{CH}_3\text{OCH}_2\text{O}_2$  spectrum has been recorded previously by Dagaut et al.<sup>10</sup> and Jenkin et al.<sup>6</sup> These determinations are

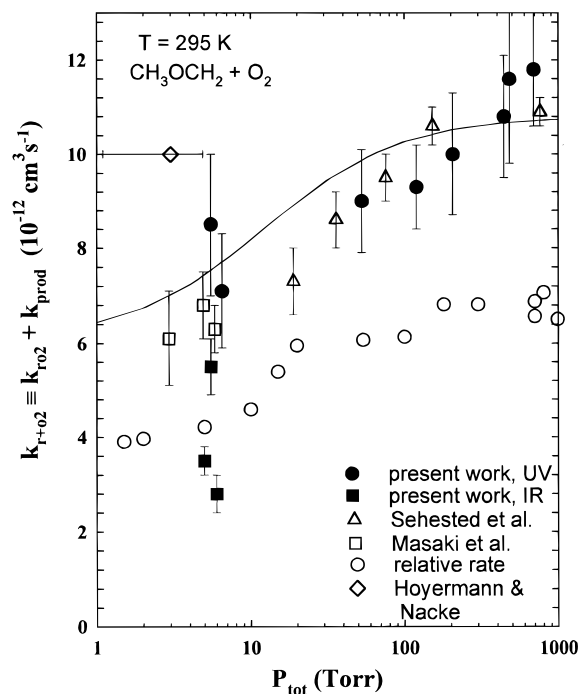
virtually identical, so only the data of Dagaut et al. are compared in Figure 1 to the present measurements. It is apparent that the spectra are in very good agreement. Both exhibit a broad structureless band peaking at 225 nm, which is typical of peroxy radicals. The work of Jenkin et al.<sup>6</sup> utilized both molecular modulation and pulsed radiolysis to generate methoxymethyl-peroxy radicals. The shape of the spectrum obtained via the former method exhibited a dependence on the  $[O_2]/[Cl_2]$  ratio, which the authors attributed to the H atom ejection in reaction 11 followed by oxygen addition to form  $HO_2$ . This radical also absorbs in the UV, at shorter wavelengths than  $CH_3OCH_2O_2$ , and thus, its presence would alter the observed composite spectrum. In the present study, the  $O_2$  concentration was too low and the time after photolysis too short for enough  $HO_2$  to form to interfere with the  $CH_3OCH_2O_2$  spectrum. Most of the previous measurements were made near atmospheric pressure; therefore, effects that the formaldehyde/OH channel of the  $CH_3OCH_2 + O_2$  reaction might have on the apparent  $CH_3OCH_2O_2$  were avoided.

**B. Chain Reaction.** The investigation of the Cl-initiated chain reaction between dimethyl ether and chlorine was carried out under conditions such that the radical population following photolysis was dominated by  $CH_3OCH_2$ . This introduces two simplifications into the reaction mechanism: first, radical-radical reactions other than the self-reaction of the methoxymethyl radical are of negligible importance and, second, precise knowledge of the rate constant for the  $Cl + CH_3OCH_3$  reaction is not necessary. The mechanism is therefore well approximated by two reactions, the self-reaction of  $CH_3OCH_2$  and its reaction with molecular chlorine. By simultaneously fitting the chlorine and methoxymethyl concentration profiles, the rate constants for these two reactions could be determined. Independent verification of the self-reaction rate constant was provided by the experiments utilizing phosgene photolysis to generate  $CH_3OCH_2$ , under conditions in which the self reaction represented the dominant reaction of this radical.

The results for  $k_{r+r}$  are compared in Figure 6 to previous room-temperature determinations by Sehested et al.<sup>11</sup> and Hoyermann et al.<sup>12</sup> The present rate constants are intermediate to the previous versions and agree with both within the combined error bars. Our measurements show  $k_{r+r}$  to be independent of pressure between 25 and 400 Torr. This is consistent with the small difference between the value of  $k_{r+r}$  obtained by Hoyermann et al. at 1–4 Torr total pressure versus the value obtained at 1 atm of  $SF_6$  by Sehested et al. The latter authors observed no systematic variation of  $k_{r+r}$  with temperature over the 296–523 K range. We find the self-reaction to exhibit a small negative temperature dependence with  $k_{r+r} = (1.08^{+0.6}_{-0.5}) \times 10^{-11} e^{(200 \pm 100)/T} \text{ cm}^3 \text{ s}^{-1}$ . This expression exhibits only a 35% change over the temperature extremes of the Sehested et al.<sup>11</sup> study and, thus, may be obscured within their data scatter.

A direct investigation of the  $CH_3OCH_2 + Cl_2$  reaction has not, to our knowledge, been previously reported, although the relative rate with respect to  $O_2$  has been measured.<sup>3</sup> Within the scope of our measurements, between 25 and 400 Torr, the reaction appears to be pressure independent, as expected for a bimolecular reaction. We find it to have a negative temperature dependence, given by  $k_{r+Cl_2} = (1.8^{+0.7}_{-0.5}) \times 10^{-11} e^{(360 \pm 120)/T} \text{ cm}^3 \text{ s}^{-1}$ . Negative temperature dependences have been observed before for this type of reaction, e.g., the  $iso-C_3H_7 + Cl_2$  reaction.<sup>13</sup>

**C.  $O_2$  Reaction.** The addition of  $O_2$  to form a peroxy radical is ubiquitous among organic radicals. Above about 100 Torr, the methoxymethyl radical, too, undergoes this pressure dependent reaction. Where this radical differs from others of its



**Figure 15.** Pressure dependence of the reaction between  $CH_3OCH_2$  and  $O_2$  at 295 K. The present results are compared to previous direct and indirect measurements of  $k_{r+O_2}$ . The relative rate data of Sehested et al.<sup>3</sup> are placed on an absolute scale using our determination of  $k_{r+Cl_2}$ . The solid line is a fit of our data to the modified Lindemann mechanism, eqs 14–16.

type, however, is in its low-pressure behavior, in which a reaction channel forming hydroxyl radicals and formaldehyde becomes important. This reaction was posited by Sehested et al.<sup>3</sup> to explain the increase with decreasing pressure of formaldehyde product from the chlorine-initiated photooxidation of dimethyl ether. It is confirmed here by the direct, time-resolved, observation of both the OH radical and formaldehyde products. However, it was apparently overlooked in the previous low-pressure investigations of the  $CH_3OCH_2 + O_2$  reaction by Hoyermann et al.<sup>12</sup> and Masaki et al.<sup>14</sup> Both groups used mass spectrometry to follow the reaction kinetics, yet reported observing only the peroxy radical product. This is perhaps understandable in the work of Masaki et al.,<sup>14</sup> since they employed photoionization by a Xe resonance lamp (8.44 eV), presumably to avoid ionizing the dimethyl ether parent compound (IP 9.96 eV), and, thus, would have missed the formation of formaldehyde (IP 10.88 eV). It is unclear why this channel was not observed by Hoyermann et al.,<sup>12</sup> who utilized electron impact ionization (energy of 10–29 eV).

The present measurements of  $k_{r+O_2}$  at high pressures ( $P_{tot} > \sim 100$  Torr) are in very good agreement with the recently reported values of Sehested et al.,<sup>11</sup> as evident from the comparison made in Figure 15 (although it is not clear if they accounted for reaction 9 in their analysis). It is interesting that both sets of rate constants exhibit nearly the same small pressure dependence in spite of the fact that one set utilized a bath gas of  $N_2$  whereas the other employed  $SF_6$ . Our UV measurements of  $k_{r+O_2}$  at low pressure ( $\sim 5$  Torr) agree well with those of Masaki et al.,<sup>14</sup> but are somewhat smaller than the value reported by Hoyermann et al.<sup>12</sup> However, this may be somewhat fortuitous owing to the omission of channel 1b from the reaction mechanism by the latter groups. In fact, substituting the experimental conditions of Masaki et al.<sup>14</sup> into the model of Table 4 leads to a predicted  $CH_3OCH_2$  loss that mimics an exponential decay, although one that decays to a constant

nonzero offset, with an apparent rate constant comparable to the true value.

Two other sets of measurements shown in Figure 15 deserve comment. First are the values of  $k_{r+o2}$  derived from the rate of formaldehyde production. That they are smaller than those from the UV measurements is attributed to vibrational excitation of the nascent  $\text{CH}_2\text{O}$ , which makes a fraction of this product initially transparent to the IR probe. Its subsequent vibrational relaxation causes an apparent formaldehyde appearance rate that is slower than the actual formation rate. Second are rate constants derived from the relative rate determinations<sup>3</sup> of  $k_{r+o2}/k_{r+cl2}$  by scaling them with the current measurement of  $k_{r+cl2}$ . These values underestimate the kinetically derived values of  $k_{r+o2}$  by about 30%. While the agreement between direct and relative rate measurements is reasonably good, it does stretch the combined error bars. The origin of the discrepancy remains uncertain. Because of the good agreement between the various direct determinations of  $k_{r+o2}$ , this is an unlikely source of the discrepancy. This leaves the present evaluation of  $k_{r+cl2}$  and the relative rate measurement as candidates. Were the discrepancies to arise from  $k_{r+cl2}$ , its already large value of  $6.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ , as compared to other  $\text{R} + \text{Cl}_2$  reactions, would have to be elevated to about  $1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ . Alternatively, there may exist some, as of yet unknown, subtlety concerning the relative rate experiments.

Assuming that both channels 1a and 1b proceed through an intermediate complex that is either stabilized or dissociates allows, via a Lindemann analysis, the pressure dependence of the reaction to be parametrized according to

$$k_{ro2} \equiv k_{1a} = \frac{k_{ro2,0}[M]}{1 + k_{ro2,0}[M]/k_{ro2,\infty}} \quad (14)$$

$$k_{prod} \equiv k_{1b} = \frac{k_{prod,0}}{1 + k_{ro2,0}[M]/k_{ro2,\infty}} \quad (15)$$

where  $k_{ro2,0}$  is a three-body rate constant that depends on the nature of the bath gas (here  $\text{N}_2$ ), and  $k_{ro2,\infty}$  is the high-pressure limit. A fit of  $k_{r+o2} = k_{ro2} + k_{prod}$  to our pressure dependent data in Figure 15 leads to values for  $k_{ro2,0}$  and  $k_{prod,0}$  of  $1.3 \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$  and  $7.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , respectively. However,  $f$ , the branching fraction for channel 1b, is given by

$$f = \frac{1}{1 + k_{ro2,0}[M]/k_{prod,0}} \quad (16)$$

and fits to eq 16 of the formaldehyde yield pressure dependence in Figure 14 give  $k_{ro2,0}/k_{prod,0} = 4.3 \times 10^{-18} \text{ cm}^3$ . Clearly, this ratio is incompatible with the individual parameters deduced from the pressure dependence of  $k_{r+o2}$  in Figure 15. This problem is resolved by noting that the three-parameter fits of  $k_{r+o2}$  to eqs 14 and 15 are insensitive to the choice of  $k_{ro2,0}$  and, consequently, that this parameter is essentially indeterminate within the accuracy of the measured rate constants.  $k_{prod,0}$  and  $k_{ro2,\infty}$ , on the other hand, are fit with reasonable accuracy. Therefore,  $k_{ro2,0}$  is deduced from fitting the formaldehyde yield to eq 16. At 295 K the results are  $k_{ro2,0} = (2.6 \pm 0.9) \times 10^{-29} \text{ cm}^6 \text{ s}^{-1}$ ,  $k_{ro2,\infty} = (11 \pm 1) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ , and  $k_{prod,0} = (6 \pm 2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . The solid line in Figure 15 represents the predicted pressure dependence of  $k_{r+o2}$  based on these parameters.

Sehested et al.<sup>11</sup> also fit the pressure dependence of the  $k_{r+o2}$  rate constant by combining their high-pressure data with the low-pressure rate constants of Masaki et al.<sup>14</sup> Their values of  $(11.4 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  and  $(6.0 \pm 0.5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$

for  $k_{ro2,\infty}$  and  $k_{prod,0}$ , respectively, are in very good agreement with the present results, with the caveat that the low-pressure rate constants were determined without consideration of reaction 1b. Their value for  $k_{ro2,0}$  of  $(9.4 \pm 4.2) \times 10^{-30} \text{ cm}^6 \text{ s}^{-1}$  is well below our determination; however, it too suffers from the data being insensitive to this parameter. It is clearly too small since a prediction of the formaldehyde yield based on this value for  $k_{ro2,0}$  gives  $k_{ro2,0}/k_{prod,0} = 1.6 \times 10^{-18} \text{ cm}^3$ , a value nearly one-third that required to fit the formaldehyde yield in Figure 14.

Including the present work, there are three determinations of the temperature dependence of the  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  reaction; however, all three are measured under different conditions. Hoyermann et al.<sup>12</sup> examined the reaction at a total pressure of about 4 Torr, finding a temperature dependence given by  $5.6 \times 10^{-13} e^{855/T} \text{ cm}^3 \text{ s}^{-1}$ . Unfortunately the interpretation of this result is questionable since they omitted channel 1b. Sehested et al.<sup>11</sup> performed their experiments at 18 bar and over a range of 296–523 K arriving at a value of  $(1.07 \pm 0.08) \times 10^{-11} e^{(46 \pm 27)/T} \text{ cm}^3 \text{ s}^{-1}$  for  $k_{r+o2}$ . Our results, near the high-pressure limit, give  $k_{r+o2} = (3.1_{-0.8}^{+1.0}) \times 10^{-12} e^{(326 \pm 80)/T} \text{ cm}^3 \text{ s}^{-1}$ .

Measurements of  $k_{ro2,0}/k_{prod,0}$  at 230, 295, and 350 K yield lower limits of  $4.8 \times 10^{-18}$ ,  $4.3 \times 10^{-18}$ , and  $2.9 \times 10^{-18} \text{ cm}^3$ , respectively. At a constant pressure, the branching fraction for channel 1b increases with increasing temperature. This is consistent with the  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  reaction proceeding through a  $\text{CH}_3\text{OCH}_2\text{O}_2^*$  complex. As the temperature is raised, the extra available thermal energy enhances dissociation of the complex into the hydroxyl and formaldehyde products.

**D. Atmospheric and Diesel Fuel Implications.** Under atmospheric conditions the methoxymethyl radical behaves as a simple organic radical; namely, it adds oxygen to form the corresponding peroxy radical. The predominant removal pathway for this radical will likely involve its reaction with NO to produce  $\text{CH}_3\text{OCH}_2\text{O}$ . The latter molecule either reacts with  $\text{O}_2$  or expels a hydrogen atom, in either case producing  $\text{HO}_2$  and methylformate. The formaldehyde/OH channel is a minor one at pressures above 100 Torr. As the inset to Figure 14 shows, this remains true over the 230–350 K temperature range. Consequently the formation of formaldehyde from channel 1b during the atmospheric degradation of dimethyl ether should be of only minor importance.

This conclusion about the impact of the formaldehyde channel is predicated on the assumption that the methoxymethylperoxy radical is thermally stable. As the temperature is increased beyond 350 K toward combustion levels, reaction 1a will become reversible. When this happens, it will dramatically affect the net hydroxyl radical formation, even at “high” pressure, and, hence, the combustion of dimethyl ether. Instead of forming the relatively unreactive peroxy radical, the  $\text{CH}_3\text{OCH}_2 + \text{O}_2$  reaction will form the more reactive hydroxyl radical, which will consume additional dimethyl ether, generate more heat, and, thereby, engender combustion. While this provides a plausible scenario for the high cetane number of dimethyl ether, additional experiments are needed to confirm the high-temperature behavior of reaction 1.

## Conclusion

A detailed kinetic investigation of the chlorine-initiated oxidation of dimethyl ether has been presented. A combination of time-resolved UV spectroscopy and transient IR absorption techniques have been brought to bear on this problem. Recording the entire UV spectrum of the reaction mixture as a function of time allows us to disentangle contributions arising from the principal species of interest,  $\text{CH}_3\text{OCH}_2$  and  $\text{CH}_3\text{OCH}_2\text{O}_2$ , as

well as those of potentially interfering contributions, such as molecular chlorine, dimethyl ether, and  $\text{CH}_3\text{OCH}_2\text{Cl}$ . Fitting the proposed reaction model to both concentration versus time profiles increases confidence in the reported rate constants.

One of the primary results is the direct detection of the hydroxyl radical and formaldehyde, thereby confirming a competition between addition and rearrangement/dissociation channels for the reaction between methoxymethyl radicals and molecular oxygen. This may begin to explain why dimethyl ether has good compression ignition characteristics, whereas other ethers are used as octane-enhancing fuel additives.

**Acknowledgment.** We thank E. W. Kaiser and T. J. Wallington for igniting our interest in the dimethyl ether study and for helpful discussions when the interpretation of experiments got a bit complicated.

#### References and Notes

(1) Leppard, W. R. *SAE Trans.* **1991**, 912313.

- (2) Kapus, P. E.; Cartellieri, W. P. *SAE Trans.* **1995**, 952754.  
(3) Sehested, J.; Møgelberg, T.; Wallington, T. J.; Kaiser, E. W.; Nielsen, O. J. *J. Phys. Chem.* **1996**, *100*, 17218.  
(4) Maricq, M. M.; Szente, J. J. *J. Phys. Chem.* **1992**, *96*, 10862.  
(5) Maricq, M. M.; Szente, J. J.; Kaiser, E. W. *J. Phys. Chem.* **1993**, *97*, 7970.  
(6) Jenkin, M. E.; Hayman, G. D.; Wallington, T. J.; Hurley, M. D.; Ball, J. C.; Nielsen, O. J.; Ellermann, T. J. *J. Phys. Chem.* **1993**, *97*, 11712.  
(7) Maricq, M. M.; Wallington, T. J. *J. Phys. Chem.* **1992**, *96*, 986.  
(8) Mallard, W. G.; Westley, F.; Herron, J. T.; Hampson, R. F. *NIST Chemical Kinetics Database Ver. 6.0*; NIST Standard Reference Data: Gaithersburg, MD, 1994.  
(9) Langer, S.; Ljuscgröm, E.; Ellermann, T.; Nielsen, O. J.; Sehested, J. *Chem. Phys. Lett.* **1995**, *240*, 53.  
(10) Dagaut, P.; Wallington, T. J.; Kurylo, M. J. *J. Photochem. Photobiol.* **1989**, *48*, 187.  
(11) Sehested, J.; Sehested, K.; Platz, J.; Egsgaard, H.; Nielsen, O. J. *J. Phys. Chem.*, submitted.  
(12) Hoyermann, K.; Nacke, F. *Twenty Sixth International Symposium on Combustion*; Napoli, July 1996.  
(13) Timonen, R. S.; Gutman, D. *J. Phys. Chem.* **1986**, *90*, 2987.  
(14) Masaki, A.; Tsunashima, S.; Washida, N. *J. Phys. Chem.* **1995**, *99*, 13126.