



# The thermal decomposition of CH3CI using the Clatom absorption method and the bimolecular rate constant for O+CH3 (1609–2002 K) with a pyrolysis photolysis shock tube technique

K. P. Lim and J. V. Michael

Citation: The Journal of Chemical Physics **98**, 3919 (1993); doi: 10.1063/1.464019 View online: http://dx.doi.org/10.1063/1.464019 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/98/5?ver=pdfcov Published by the AIP Publishing

# Articles you may be interested in

Rate constants for the reactions H+O2 $\rightarrow$ OH+O and D+O2 $\rightarrow$ OD+O over the temperature range 1085–2278 K by the laser photolysis–shock tube technique J. Chem. Phys. **95**, 262 (1991); 10.1063/1.461483

Rate constants for the reaction, H+D2 $\rightarrow$ HD+D, over the temperature range, 724–2061 K, by the flash photolysisshock tube technique J. Chem. Phys. **92**, 3394 (1990); 10.1063/1.457850

Rate constants for the reaction O+D2→OD+D by the flash photolysis–shock tube technique over the temperature range 825–2487 K: The H2 to D2 isotope effect J. Chem. Phys. **90**, 189 (1989); 10.1063/1.456513

The kinetics and thermodynamics of the reaction H+NH3NH2+H2 by the flash photolysis–shock tube technique: Determination of the equilibrium constant, the rate constant for the back reaction, and the enthalpy of formation of the amidogen radical J. Chem. Phys. **88**, 830 (1988); 10.1063/1.454162

Shock tube study of the thermal decomposition of O3 from 1000 to 3000°K J. Chem. Phys. **62**, 802 (1975); 10.1063/1.430530



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 147.143.2.5 On: Sat. 20 Dec 2014 16:36:49

# The thermal decomposition of $CH_3CI$ using the Cl-atom absorption method and the bimolecular rate constant for $O+CH_3$ (1609–2002 K) with a pyrolysis photolysis-shock tube technique

K. P. Lim and J. V. Michael Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 31 August 1992; accepted 3 November 1992)

Rate constants for the thermal decomposition of CH<sub>3</sub>Cl and the atom-radical reaction  $O+CH_3$  have been measured in shock tube experiments. The decomposition of CH<sub>3</sub>Cl, at three loading pressures, has been carried out between 1663–2059 K with mixtures that varied from 1.25 to 24.9 ppm in Ar. The first-order rate constant  $k_1=1.21\times10^{10}$   $\times \exp(-27\,838$  K/T) s<sup>-1</sup> describes the experimental results to within  $\pm 29\%$  at the one standard deviation level. The bimolecular rate experiment has then been carried out over the temperature range 1609–2002 K using mixtures of SO<sub>2</sub> (49.9 ppm) and CH<sub>3</sub>Cl (5.14 and 8.2 ppm) in Ar. The technique first involves allowing the thermal decomposition to proceed forming CH<sub>3</sub> radicals, and this is then followed by delayed photolysis of SO<sub>2</sub> forming the O-atom species. This new method is called the pyrolysis photolysis-shock tube (PyPh-ST) technique. A reaction mechanism had to be used to simulate the measured O-atom profiles for the various experimental conditions, and the bimolecular rate constant was found to be temperature independent with a value of  $k_2=1.4\times10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Reactions (1) and (2) are both theoretically discussed.

# INTRODUCTION

The importance of mechanism in explaining the chemistry occuring in combustion systems is well known.<sup>1-8</sup> Even though the methods for numerical analysis, with attendant assessment of sensitivity factors for the various chemical processes,<sup>9-11</sup> are well advanced, mechanistic predictions ultimately rely on an accurate knowledge of both the products and rate constants for the processes involved in such a combustion system. This realization has prompted the development of experimental methods for measuring rate constants and products of chemical reactions under conditions that are commonly encountered in combustion. These methods have mostly concentrated on unimolecular processes (usually measured with shock tube methods<sup>12</sup>) and bimolecular reactions of atomic or radical species with stable molecules. A variety of techniques have been used for the latter type experiment;<sup>13</sup> however, for the combustion regime, the shock tube technique has usually been the method of choice.<sup>12,14</sup> Even though atom with radical or radical with radical reaction rate constants are known to be important and have been estimated by simulating relatively high density reactive systems, the development of more direct methods has been neglected, simply because of the difficulty of preparing and measuring known concentrations of unstable species. It is this neglect that has supplied the motivation for the present study.

In this work, the primary goal is to measure the rate constant for the  $O+CH_3$  reaction at combustion temperatures by as direct a means as possible. It is therefore necessary to devise a method for preparing  $CH_3$  radicals and O atoms under controlled conditions. Because of the high detection sensitivity, the atomic resonance absorption spectrometric (ARAS) method has been the method of choice in this laboratory.<sup>14</sup> This high sensitivity has allowed experiments to be performed under conditions where secondary chemistry contributes little or not at all. Hence, in the present case, the unimolecular decomposition of  $CH_3Cl$ has been chosen as the source of  $CH_3$  radicals and the simultaneous formation of Cl atoms then allows for the extent of decomposition to be assessed by using the Cl atom ARAS method of detection.

In preparation for the  $O+CH_3$  study, it has been necessary to characterize the Cl atom ARAS method and also to measure the rate constants for the thermal decomposition of CH<sub>3</sub>Cl. We have accordingly determined the curve of growth for Cl atoms and the rate constants for the reaction

$$CH_3Cl \rightarrow CH_3 + Cl$$
 (1)

over the temperature range 1663–2059 K. With this prior knowledge, the delayed excimer laser photolysis of  $SO_2$  then supplies the O atoms for the primary study; i.e.,

$$O+CH_3 \rightarrow \text{products.}$$
 (2)

 $[O]_t$  is measured quantitatively again with the ARAS technique, and from the measured profiles, the values of  $k_2$  can be assessed for the temperature range 1609–2002 K. Since the method first requires the thermal pyrolysis of CH<sub>3</sub>Cl followed by the delayed photolysis of SO<sub>2</sub>, we call it the pyrolysis photolysis-shock tube (PyPh-ST) technique.

# EXPERIMENT

The experimental methods used in the present investigation have been described in detail previously.<sup>14</sup> Therefore, only the procedures that are directly pertinent to the present investigation are given below.

#### Apparatus

The shock tube consisted of a 7 m (o.d. 4 in.) 304 stainless steel tube with a driver chamber. These sections were separated by a thin aluminum diaphragm (4 mil, unscored 1100-H18). The tube was routinely pumped to  $< 10^{-8}$  Torr between experiments by an Edwards Vacuum Products, model CR100P packaged pumping system. Eight pressure transducers (PCB Piezotronics, Inc., model 1132A), placed at fixed intervals, measured the incident shock velocity, and final temperature and density in the reflected shock wave regime were calculated from the incident velocity after correction for the nonidealities due to boundary layer perturbations.<sup>14</sup> The photometer system was radially located 6 cm from the endplate and had an optical path length of 9.94 cm. Transmittances from the resonance lamps were measured with an EMR G14 solar blind photomultiplier tube. The signal was then recorded by a Nicolet 4094C digital oscilloscope. Mixture compositions and reactant pressures were measured with an MKS Baratron capacitance manometer.

## CI Atom ARAS detection system

The Cl atom resonance lamp configuration was similar to the one used by Whytock *et al.*<sup>15</sup> Cl atom resonance radiation was produced by flowing a mixture of Cl<sub>2</sub> in He through a microwave discharge lamp. The lamp was operated at 50 W microwave power with  $X_{Cl_2} = 1 \times 10^{-3}$  at a flow pressure of approximately 1.5 Torr. As discussed by Whytock *et al.*<sup>15</sup> and more thoroughly by Clyne and Nip,<sup>16</sup> this lamp configuration gives a multiplet structure that is somewhat reversed. Resonance radiation was observed through a BaF<sub>2</sub> filter without wavelength resolution.

In earlier work from this laboratory, the fraction of resonance radiation in the resonance lamp has been routinely determined with an atomic filter system.<sup>14</sup> In the present case, this filter would consist of a fast flow system of Cl<sub>2</sub> in He that was subjected to microwave dissociation upstream from the optical path. This configuration was tested; however, the wall recombination of Cl atoms in the fast flow system was not reproducible and gave ambiguous results. Therefore, the thermal decomposition of large concentrations of carbon tetrachloride CCl<sub>4</sub> at high temperatures (where dissociation was extensive) was used in order to obtain the fraction of light that is resonance radiation. To determine the fraction, several fairly high CCl<sub>4</sub> concentration mixtures were shock heated to temperatures just below those necessary for thermal decomposition. Cl atoms were not formed and therefore did not absorb the resonance light. This procedure was used to determine the overall absorption coefficient of CCl<sub>4</sub> at the Cl atom resonance radiation wavelengths. Since [CCl<sub>4</sub>]<sub>0</sub> was known in these preliminary experiments, the measurement could then be used to calculate the  $I_0$  for subsequent higher temperature experiments, where copious quantities of Cl atoms were produced on shock heating. At the highest  $[CCl_4]_0$ used, the fraction of light remaining after absorption was  $14\% \pm 2\%$  of that before decomposition; i.e., 86% of the light from the resonance lamp was resonance radiation.



FIG. 1. A typical experimental record showing decreasing ARAS signal with time as Cl atoms are forming from the decomposition of CH<sub>3</sub>Cl. T=1790 K, P=604 Torr,  $\rho=3.259\times10^{18}$  with [CH<sub>3</sub>Cl]= $2.065\times10^{13}$  molecules cm<sup>-3</sup>; i.e.,  $X_{\rm CH_3Cl}=6.336\times10^{-6}$ .

The thermal decomposition of  $CH_3Cl$  was then studied by observing Cl atom formation.

Figure 1 is a typical experimental record from the thermal decomposition of CH<sub>3</sub>Cl showing a decreasing ARAS signal as Cl atoms form with time. Since the fraction of light that is resonance radiation is known, absorbance by Cl atoms [where (ABS)<sub>t</sub>=  $-\ln(I_t/I_0)$ ] can be determined. The thermal decompositions of three molecules CCl<sub>4</sub>, Cl<sub>2</sub>, and CH<sub>3</sub>Cl were then investigated at sufficiently high temperatures, so that steady state values (ABS)<sub>∞</sub> were reached. These experiments were carried out with varying initial reactant concentrations and the absorbance values are plotted against the reactant concentrations as shown in Fig. 2. These data represent raw yields of Cl atoms.

In order to obtain the curve of growth for Cl atoms, data of the type shown in Fig. 2 have to be corrected for secondary chemistry (stoichiometric factors) if such secondary chemistry is complicating. There are no such complicating reactions in the thermal decomposition of Cl<sub>2</sub> and the signal level should therefore correspond to the case where two atoms are produced for every one molecule that decomposes. In the upper panel of Fig. 2, the results for  $Cl_2$ are compared to those for CCl<sub>4</sub>. Cl<sub>2</sub> is highly reactive and might be removed by reaction with the metal surface of the shock tube before the gas is shock heated. It was therefore probable that some loss of Cl<sub>2</sub> molecules might have occurred, and this may explain why the results for Cl<sub>2</sub> lie below those for CCl<sub>4</sub>. In any case, the comparison shows that at least two Cl atoms are produced for every one CCl<sub>4</sub> molecule that decomposes. In CCl<sub>4</sub>, the subsequent chemistry at high temperatures of the initial radical that is produced, namely CCl<sub>3</sub>, is speculative, and the aforementioned attempt at stoichiometric correction is likewise speculative. However, the lower panel of Fig. 2 shows the



FIG. 2.  $(ABS)_{\infty}$  for Cl atom absorption from the decompositions of Cl<sub>2</sub>, CCl<sub>4</sub>, and CH<sub>3</sub>Cl. The top panel (top abscissa) shows the data from [Cl<sub>2</sub>] ( $\blacktriangle$ ) and [CCl<sub>4</sub>] ( $\bigcirc$ ) with almost the same behavior, thereby implying that the dissociation of CCl<sub>4</sub> gives at least the same [Cl]<sub> $\infty$ </sub> as Cl<sub>2</sub>. When [CH<sub>3</sub>Cl] ( $\bigcirc$ ) is compared to [CCl<sub>4</sub>] ( $\bigcirc$ ) in the bottom panel (bottom abscissa), CCl<sub>4</sub> gives about twice as many Cl atoms as CH<sub>3</sub>Cl on thermal decomposition.

comparison of the CCl<sub>4</sub> and CH<sub>3</sub>Cl results at considerably lower concentrations. The line drawn through the CH<sub>3</sub>Cl set is exactly one half of that through the CCl<sub>4</sub> set. Since the  $\Delta H_{298 \text{ K}}^0$  for reaction (1) is 83.6 kcal mol<sup>-1</sup> and that for  $CH_3Cl \rightarrow {}^1CH_2 + HCl$  is 97.7 kcal mol<sup>-1</sup>,<sup>17</sup> the lowest lying dissociation products are  $CH_3 + Cl$  (i.e., one Cl atom is formed for every CH<sub>3</sub>Cl molecule that decomposes and, conversely, the recombination predominantly gives CH<sub>3</sub>Cl and not  ${}^{1}CH_{2}+HCl$ ). The comparison in Fig. 2 then suggests that exactly two Cl atoms are formed for every one CCl<sub>4</sub> molecule that decomposes. This conclusion may not be precisely correct because there is an obvious stoichiometric correction in the CH<sub>3</sub>Cl case. However, the assessment of this correction is simple since the only significant depletion reaction is the reaction between Cl atoms and CH<sub>3</sub>Cl.

We have numerically integrated an expanded mechanism [reactions (1) and (3)–(8)] shown in Table I and have calculated stoichiometric factors  $S \equiv [CI]_{\infty}^{calc} / [CH_3Cl]_0$  for the experiments shown in Fig. 2. The numerical integration for all experiments had to be carried out iteratively because the rate constants for reaction (1) also

TABLE I. The mechanism used for the rate determination of the  $O+CH_3$  reaction.

| CH <sub>3</sub> Cl→CH <sub>3</sub> +Cl | $k_1 = 1.21 \times 10^{10}$                                                                                                                                                                                                                                                                                                                                                                       |
|----------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|                                        | $\times \exp(-27\ 838\ K/T)^{a}$                                                                                                                                                                                                                                                                                                                                                                  |
| $O+CH_3 \rightarrow H_2CO+H$           |                                                                                                                                                                                                                                                                                                                                                                                                   |
| or CO+H <sub>2</sub> +H                | $k_2 = $ to be fitted                                                                                                                                                                                                                                                                                                                                                                             |
| $Cl+CH_{3}Cl\rightarrow HCl+CH_{2}Cl$  | $k_3 = 5.6 \times 10^{-11}$                                                                                                                                                                                                                                                                                                                                                                       |
|                                        | $\times \exp(-1425 \ K/T)^{b}$                                                                                                                                                                                                                                                                                                                                                                    |
| $CH_3 + CH_3 \rightarrow C_2H_6$       | $k_4(T,\rho) =$ from Walter et al. <sup>c</sup>                                                                                                                                                                                                                                                                                                                                                   |
| $CH_3 + CH_3 \rightarrow C_2H_5 + H$   | $k_5 = 1.9 \times 10^{-9}$                                                                                                                                                                                                                                                                                                                                                                        |
|                                        | $\times \exp(-10075K/T)^{d}$                                                                                                                                                                                                                                                                                                                                                                      |
| $C_2H_5 \rightarrow C_2H_4 + H$        | $k_6 = \infty$ for the present                                                                                                                                                                                                                                                                                                                                                                    |
|                                        | T range <sup>e</sup>                                                                                                                                                                                                                                                                                                                                                                              |
| $CH_3 + CH_3 \rightarrow C_2H_4 + H_2$ | $k_7 = 1.66 \times 10^{-8}$                                                                                                                                                                                                                                                                                                                                                                       |
|                                        | $\times \exp(-16556K/T)^{\mathrm{f}}$                                                                                                                                                                                                                                                                                                                                                             |
| Cl+CH <sub>3</sub> →CH <sub>3</sub> Cl | $k_8 = k_1 / K_1^g$                                                                                                                                                                                                                                                                                                                                                                               |
| $O+CH_3Cl\rightarrow OH+CH_2Cl$        | $k_9 = 2.6 \times 10^{-11} T^{0.31}$                                                                                                                                                                                                                                                                                                                                                              |
|                                        | $\times \exp(-5633 \ K/T)^{h}$                                                                                                                                                                                                                                                                                                                                                                    |
|                                        | $CH_{3}CI \rightarrow CH_{3} + CI$ $O + CH_{3} \rightarrow H_{2}CO + H$ or $CO + H_{2} + H$ $CI + CH_{3}CI \rightarrow HCI + CH_{2}CI$ $CH_{3} + CH_{3} \rightarrow C_{2}H_{6}$ $CH_{3} + CH_{3} \rightarrow C_{2}H_{5} + H$ $C_{2}H_{5} \rightarrow C_{2}H_{4} + H$ $CH_{3} + CH_{3} \rightarrow C_{2}H_{4} + H_{2}$ $CI + CH_{3} \rightarrow CH_{3}CI$ $O + CH_{3}CI \rightarrow OH + CH_{2}CI$ |

<sup>a</sup>Present determination [Eq. (3)].

<sup>b</sup>Estimated from Cl atom abstraction rate behavior and experiment (Ref. 18).

<sup>c</sup>Reference 19.

<sup>d</sup>Estimated from H atom profiles (see the text). <sup>e</sup>Reference 20. <sup>f</sup>Reference 21. <sup>g</sup>K<sub>1</sub> is given by Eq. (6).

<sup>h</sup>Reference 22.

had to be varied. Approximate values for  $k_1$  in the simulation supplied a preliminary value for  $[Cl]_{\infty}^{calc}$  from which a first estimate of the stoichiometric correction was calculated. These factors were then applied to the experiments to construct an approximate curve of growth for Cl atom absorption thereby determining an effective absorption cross section,  $\sigma_{\rm Cl \ atom}$ . This preliminary estimate of cross section was then used, keeping (ABS)  $\ll 0.12$ , to convert incident time experimental absorption data to initial [Cl]<sub>t</sub>. Comparison of  $[Cl]_t$  simulations to experiments allowed for improved values for  $k_1$  to be chosen. These new values for  $k_1$  were then used again to simulate all experiments. The recalculated estimates of [Cl]<sub>∞</sub> then gave improved stoichiometric corrections thereby giving an improved effective cross section and slightly different values for  $k_1$ . These were used in a third iteration for both  $[Cl]_{\infty}$  and  $k_1$  determinations. The process was, in general, unambiguous since, at the lower  $[CH_3Cl]_0$  (bottom panel of Fig. 2), the values of S are all nearly unity because all secondary reactions are negligible; however, at the higher values, the correction, due mostly to the Cl+CH<sub>3</sub>Cl reaction, is significant. An example of a final simulation is shown in Fig. 3. In this example, the predicted  $[Cl]_{\infty} = 0.847 [CH_3Cl]_0$ , giving an S value of 0.847. It should also be noted that the other products predicted in this illustration only amount to about 10%-15% of [CH<sub>3</sub>Cl]<sub>0</sub>, indicating again that the major reaction responsible for the correction is the Cl +CH<sub>3</sub>Cl reaction. Application of the correction procedure to all of the CH<sub>3</sub>Cl data in Fig. 2 then gives the curve of growth for Cl atoms that is shown in Fig. 4.

#### Cl atom kinetics analysis

In the Cl atom case (unlike that for H or O atoms), the curve of growth indicates significant curvature. There-



FIG. 3. A plot of reactant and product profiles from a simulation of the CH<sub>3</sub>Cl decomposition, based on the mechanism in Table I, without photolysis.  $[CH_3Cl]_0=1.660\times10^{13}$  molecules cm<sup>-3</sup> and T=1798 K. The stoichiometric correction  $S \equiv [Cl]_{\infty}^{calc}/[CH_3Cl]_0=0.847$ .

fore, kinetics experiments that proceed to high absorbances must be corrected for this nonlinear behavior. However, if the range of absorbances used in the analysis is limited to (ABS)<sub>i</sub> $\leq$ 0.12 (see the inset in Fig. 4), the curve of growth



FIG. 4. The graph correlates the Cl atom absorbance to [Cl]. This curve of growth shows significant curvature at high absorbances, but is nearly linear for  $(ABS) \leq 0.12$  (inset).



FIG. 5. An Arrhenius plot of experimentally determined first-order rate constants for the  $CH_3Cl$  decomposition in Ar at three different loading pressures.

is nearly linear and a constant value can be derived for the Cl atom absorption cross section  $\sigma_{\text{Cl atom}} = (2.37 \pm 0.08) \times 10^{-15} \text{ cm}^2$ . As mentioned above, this value was arrived at iteratively and it then supplies the scale factor to convert initial values of (ABS), into [Cl]<sub>r</sub>. Also as mentioned above, the values for  $k_1$  were varied until initial [Cl], from the simulations with the Table I mechanism and the experiments agreed. The resulting first-order values for  $k_1$  from all experiments are shown as an Arrhenius plot in Fig. 5.

## O atom production and ARAS detection

After CH<sub>3</sub>Cl had partially decomposed, the delayed 193 nm ArF excimer photolysis of SO<sub>2</sub> produced the O atoms for the study of reaction (2). Photolysis occurred through the endplate window of the shock tube in the reflected shock regime. It was important to establish that SO<sub>2</sub> itself was kinetically unreactive at the high temperatures of the kinetics experiments. Several Cl atom profiles were measured in the presence of varying [CH<sub>3</sub>Cl] and [SO<sub>2</sub>], and these were compared to those without SO2. The results showed that Cl atoms do not react with the presently used values of [SO2]. In work from this laboratory, it was earlier established that neither H nor O atoms react with SO<sub>2</sub>.<sup>23</sup> H atom profiles were also measured in the presence and absence of  $SO_2$ . Since H atoms are formed by the reaction of two CH<sub>3</sub> radicals and the results from H atom profile measurements are unaffected by the presence or absence of SO<sub>2</sub>, we conclude that CH<sub>3</sub> radicals likewise do not appreciably react with SO<sub>2</sub>. Hence, SO<sub>2</sub>, at the concentrations used here, is a spectator molecule.

The O atom photometer system used in detecting O atoms from SO<sub>2</sub> photolysis is the same as that used in previous work from this laboratory, where a calibration procedure that is based on the thermal decomposition of  $N_2O$  is described.<sup>24</sup> In the present work, the lamp configuration  $X_{O_2} = 1 \times 10^{-3}$  in 1.8 Torr of purified grade He operating at 50 W microwave power (effective lamp temperature of 490 K) has been used. The 130.2, 130.4, and 130.6 nm triplet resonance lines are isolated with a  $CaF_2$ window (transmitting  $\lambda > 125$  nm), and the fraction of the light that is resonance radiation is determined by using the previously described O atom atomic filter section method.<sup>14,25</sup> In the photolysis experiments, the optical path length is determined by the laser beam width and the window diameter ( $l=4.2\pm0.2$  cm). In the calibration experiments,<sup>24</sup> the optical path length, as noted above, was 9.94 cm, and line absorption calculations showed that the curve of growth for O atoms was slightly temperature dependent and was only slightly nonlinear. In the present work, the effective average cross section  $\sigma_{\rm O\ atom}$  was calculated for the temperature and maximum absorbance for each experiment  $[(ABS)_{max} \leq 0.3$  giving  $[O]_0 \leq 7.5 \times 10^{12}$  molecules  $cm^{-3}$ ], and this was then used as a constant scale factor to extract  $[O]_t$  from (ABS)<sub>t</sub> for the given experiment. The uncertainty in  $[O]_0$  arises from at least two sources: (1) the error in the optical path length (10% spread) and (2) the zero time extrapolation; however, the use of a constant  $\sigma_{O \text{ atom}}$  contributes another  $\pm 10\%$  error. Hence, we conclude that the values for [O]<sub>0</sub> are only absolutely accurate to  $\sim \pm 20\%$ .

#### Gases

The high purity He (99.995%) used as the driver gas was obtained from Air Products and Chemicals, Inc. Scientific grade Ar (99.9999%) used as the diluent gas in reactant mixtures was obtained from MG Industries. The ultrahigh purity grade He (99.999%) used in the resonance lamp was from Airco Industrial Gases. Research grade  $Cl_2$  (99.999%) was obtained from MG Industries and was used as received.  $CH_3Cl$  (99.5%) was from AGA Specialty Gases, and  $CCl_4$  was obtained from Mallinckrodt Specialty Chemicals Co. Both  $CCl_4$  and  $CH_3Cl$  were purified by bulb-to-bulb distillation and only the middle third was retained. Samples of  $CCl_4$  and  $CH_3Cl$  were further subjected to mass spectrometric analysis in order to verify their purities.

# RESULTS

#### Thermal decomposition of CH<sub>3</sub>CI

Thirty-six values were determined for  $k_1$  between 1663 and 2059 K at three different loading pressures. CH<sub>3</sub>Cl mixtures in Ar varied from 1.25 to 24.9 ppm for these experiments. The range of reflected shock densities varied from about 1.4 to  $3.4 \times 10^{18}$  molecules cm<sup>-3</sup> and are distinguished from one another by loading pressure in Fig. 5. It is obvious by inspection that, with the present experimental error, these data are not strongly pressure dependent; however, we do note that the lowest pressure set at 6

FIG. 6. An experimental profile of O atom decay after partial pyrolysis of CH<sub>3</sub>Cl and delayed photolysis of SO<sub>2</sub>, where the experimental conditions are T = 1798 K, P = 602 Torr,  $\rho = 3.233 \times 10^{18}$ ,  $[CH_3Cl] = 1.660 \times 10^{13}$ ,  $[SO_2] = 1.613 \times 10^{14}$ , and  $[O]_0 = 5.398 \times 10^{12}$  molecules cm<sup>-3</sup>; i.e., the same as Fig. 3. The line is a simulated fit that is based on the mechanism in Table I, including reactions (2) and (9).  $k_2 = 1.8 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> gives the best fit.

Torr lies systematically lower than the higher 15 Torr set. Even so, we have used all three data sets to describe the rate behavior with a linear least squares first-order Arrhenius expression  $k_1 = A_1 \exp(-B_1/T)$ ,

$$k_1 = 1.21 \times 10^{10} \exp(-27\ 838\ K/T)\ s^{-1},$$
 (3)

where the error in log  $A_1$  is  $\pm 0.37$  and in  $B_1$  is  $\pm 1574$  K. The points shown in Fig. 5 deviate from Eq. (3) by  $\pm 29\%$  at the one standard deviation level.

#### Rate constants for the O+CH<sub>3</sub> reaction

Figure 6 shows experimental results for O atom decay under exactly the same conditions as the simulation in Fig. 3. If the logarithm of the profile in Fig. 6 is plotted and a pseudo-first-order decay constant is extracted from the resulting graph, the value obtained is  $(1465 \pm 165)$  s<sup>-1</sup>. A naive rate constant estimate for  $O + CH_3$  can be derived by assuming that each CH<sub>3</sub>Cl molecule decomposing gives one CH<sub>3</sub> radical. Then  $k_2 \approx 1465/(1.66 \times 10^{13}) = 0.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Inspection of Fig. 3 shows that the assumption of 100% dissociation to CH<sub>3</sub> radicals is, however, not correct since there is some CH<sub>3</sub>Cl destruction by Cl atom abstraction and also CH<sub>3</sub> radicals undergo self destruction. It is therefore necessary to simulate the complete mechanism shown in Table I. With the rate constants listed in the table, reactions (1) and (3)-(8) were numerically integrated up to the delayed time for photolysis, and this supplied the initial conditions for subsequent simulations that included reactions (2) and (9) in the table. Reaction (9) has recently been measured by Ko et al.,<sup>22</sup> and therefore, only reaction (2) has to be fitted to experimental profiles. The successful simulation for the O





FIG. 7. A complete simulation for the experiment of Fig. 6 showing reactant and product profiles.  $[CH_3Cl]_t$  and  $[Cl]_t$  are nearly the same as in Fig. 3, but  $[CH_3]_t$  has decreased due to the fast reaction with O atoms. H atoms and H<sub>2</sub>CO are seen to be the major products.

TABLE II. Rate data for  $O + CH_3 \rightarrow H_2CO + H$  or  $CO + H_2 + H$ .

| P <sub>1</sub> /Torr   | $M_s^{\rm a}$       | $\rho_5/(10^{18} \mathrm{cm}^{-3})^{\mathrm{b}}$ | T∕K <sup>♭</sup>   | $k_2/(10^{-10} \mathrm{cm}^3 \mathrm{s}^{-1})^c$ |
|------------------------|---------------------|--------------------------------------------------|--------------------|--------------------------------------------------|
| $X_{CH_2CI} = 5.1$     | 36×10 <sup>-6</sup> | $X_{SO_2} = 4.989$                               |                    |                                                  |
| 15.89                  | 2.726               | 3.277                                            | 1818               | 1.3                                              |
| 15.89                  | 2.722               | 3.273                                            | 1813               | 1.3                                              |
| 15.83                  | 2.707               | 3.246                                            | 1795               | 1.3                                              |
| 15.83                  | 2.705               | 3.233                                            | 1798               | 1.8                                              |
| 10.90                  | 2.775               | 2.312                                            | 1885               | 1.1                                              |
| 10.87                  | 2.866               | 2.367                                            | 2002               | 1.3                                              |
| 10.91                  | 2.542               | 2.132                                            | 1609               | 1.3                                              |
| 10.82                  | 2.670               | 2.212                                            | 1761               | 1.1                                              |
| $X_{\rm CH_3Cl} = 8.1$ | 82×10 <sup>-6</sup> | $X_{SO_2} = 4.98$                                | 4×10 <sup>-5</sup> |                                                  |
| 15.92                  | 2.851               | 3.398                                            | 1972               | 1.2                                              |
| 15.87                  | 2.669               | 3.217                                            | 1750               | 1.5                                              |
| 15.86                  | 2.673               | 3.218                                            | 1754               | 1.2                                              |
| 15.95                  | 2.754               | 3.316                                            | 1853               | 2.0                                              |
| 10.95                  | 2.772               | 2.313                                            | 1888               | 1.8                                              |
| 10.76                  | 2.682               | 2.209                                            | 1776               | 1.0                                              |
| 10.91                  | 2.641               | 2.209                                            | 1726               | 1.5                                              |
|                        |                     |                                                  |                    | Average= $1.4\pm0.3$                             |

<sup>a</sup>The error in measuring the Mach number  $M_s$  is typically 0.5%–1.0% at the one standard deviation level.

<sup>b</sup>Quantities with the subscript 5 refer to the thermodynamic state of the gas in the reflected shock region.

°The rate constants are derived, as described in the text, from fits to O atom profiles. An illustration is shown in Fig. 6. The estimated accuracy in fitting is  $\pm 10\%$  of the derived value.

atom profile of Fig. 6 (solid line) is shown in Fig. 7, the best fit value being  $k_2 = 1.8 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

Several additional experiments under a variety of conditions have been performed, and O atom profiles have been fitted by varying  $k_2$ . The resulting conditions and best fit values for 15 experiments are presented in Table II, where a temperature independent value of  $k_2 = (1.4 \pm 0.3)$  $\times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is derived for the range  $1609 \le T \le 2002$  K.

### DISCUSSION

## CH<sub>3</sub>Cl thermal decomposition

The rate constant for reaction (1) has been previously measured in a shock tube investigation by observing CH<sub>3</sub> radical buildup with UV absorption spectrometry.<sup>26</sup> At comparable densities, these results do not agree with the present work as given by Eq. (3) and Fig. 5. The discrepancy is about 15 to 20 times lower than the present results. The main difference in the two studies is that substantial corrections for secondary reactions had to be made by Kondo *et al.*<sup>26</sup> since high  $[CH_3Cl]_0$  was necessary in order to form enough  $[CH_3]$  for observation. In the present case,  $[CH_3Cl]_0$  was much lower, and initial rates of Cl atom formation were observed under conditions where secondary reaction complications were minimal.

In the study of reaction (2),  $O+CH_3$ , the temporal behavior of  $CH_3$  radicals is totally determined by the mechanism shown in Table I, where the rate of decomposition of  $CH_3Cl$  is given by the first-order expression (3). The question arises as to whether Eq. (3) is a reasonable result. Kondo *et al.*<sup>26</sup> examined the decomposition using the Troe theoretical formalism<sup>9,27-30</sup> and concluded that their results were in accord with the predictions of this theory if  $\beta_c \approx 0.02-0.03$ . This  $\beta_c$  implies  $-\Delta E_{\rm all} \approx 50 \text{ cm}^{-1}$ (giving  $\Delta E_{\rm down} \approx 310 \text{ cm}^{-1}$ ). Since a disagreement exists between the present work and that of Kondo *et al.*,<sup>26</sup> a revision in the relatively low  $\beta_c$  values will undoubtedly be involved.

We have also used the semiempirical form of Troe theory9,27-30 to calculate theoretical rate constants for reaction (1). Since there are no potential energy surface calculations for the present case, we have not used flexible transition state theory.<sup>31,32</sup> Rather, it is our opinion that when surfaces for a reaction with a zero potential energy barrier in one direction are nonexistent, the best choice of transition state is the Lennard-Jones (LJ) complex, where the LJ distance between the combining species is taken to be the reaction coordinate and all rotational degrees of freedom in each of the combining species are considered to be free. This choice of transition state is based on experiment because transport property measurements are used to determine Lennard-Jones parameters, and these parameters can then be used to make transport property predictions for any set of gases. These predictions generally agree, within a few percent, with experimental values.<sup>33</sup> Using conventional transition state theory, this model will always give, as the high pressure limit for the recombination of the two species making up the complex, the collision rate constant with electronic degeneracy factors included

$$k_{\rm coll} = (g^{\ddagger}/g_1g_2)r_{12}^2(8\pi kT/\mu)^{1/2}\exp(E/kT).$$
(4)

TABLE III. Parameters for the theoretical evaluation of  $CH_3Cl \rightarrow CH_3+Cl$ .

| <i>T/</i> K | F <sub>anh</sub> | F <sub>rot</sub> | F <sub>E</sub> | $k_{10}^{sc}/(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ | S <sub>K</sub> | B <sub>K</sub> | β <sub>c</sub> | F <sub>cent</sub> |
|-------------|------------------|------------------|----------------|------------------------------------------------------------------|----------------|----------------|----------------|-------------------|
| 1600        | 1.07             | 2.46             | 1.31           | 7.64(-16)                                                        | 4.81           | 21.2           | 0.275          | 0.424             |
| 1700        | 1.07             | 2.40             | 1.33           | 2.94(-15)                                                        | 4.94           | 21.0           | 0.254          | 0.423             |
| 1800        | 1.07             | 2.34             | 1.36           | 9.52(-15)                                                        | 5.05           | 20.8           | 0.235          | 0.424             |
| 1900        | 1.07             | 2.29             | 1.38           | 2.68(-14)                                                        | 5.16           | 20.6           | 0.218          | 0.425             |
| 2000        | 1.07             | 2.23             | 1.41           | 6.68(-14)                                                        | 5.27           | 20.4           | 0.202          | 0.427             |
| 2100        | 1.07             | 2.18             | 1.44           | 1.51(-13)                                                        | 5.37           | 20.1           | 0.187          | 0.430             |

Equation (4) can then be corrected with the LJ model if the LJ parameters are known. With the assumption that  $\sigma_{CH_3} \simeq \sigma_{CH_4} = 3.809$  Å and  $\epsilon_{CH_3}/k \simeq \epsilon_{CH_4}/k = 148.1$  K,<sup>33</sup> and previous estimates for Cl atoms  $\sigma_{Cl}=2.34$  Å and  $\epsilon_{Cl}/k=119$  K,<sup>34,35</sup> Eq. (4) becomes

$$k_{-1LJ} = (g^{\ddagger}/g_1g_2)\sigma_{12}^2\Omega(2,2)^*(8\pi kT/\mu)^{1/2}\exp(\epsilon_{12}/kT).$$
(5)

With  $g^{\ddagger}=1$ ,  $g_{CH_3}=2$ , and  $g_{Cl}=2\{2+\exp[-hc(882.36 \text{ cm}^{-1})/kT]\}$ , Eq. (5) has been evaluated between 1600 and 2100 K giving a nearly constant value of  $(4.8\pm0.1) \times 10^{-11} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup>. The value for the high pressure dissociation rate constant is then easily calculated as  $k_{1\infty}=k_{-1LJ}K_1$ . Equilibrium constants  $K_1$  for the process have been directly calculated from molecular constants and they agree with the values from the JANAF thermochemical tables;<sup>17</sup> i.e., for  $1600 \leqslant T \leqslant 2100$  K,

$$K_1 = 2.489 \times 10^{25} \exp(-41\ 104\ K/T)$$
 molecules cm<sup>-3</sup>
(6)

to within  $\pm 0.5\%$ . Combining Eqs. (5) and (6) gives the result

$$k_{1\infty} = 1.40 \times 10^{15} \exp(-41\ 373\ K/T)\ s^{-1}$$
 (7)

for the T range. Weissman and Benson<sup>36</sup> have previously estimated  $k_{1\infty} = 2.51 \times 10^{15} \exp(-42.073 \ K/T) \ s^{-1}$  and their result is negligibly different, being only 16–30% higher than Eq. (7).

The theory of Troe and co-workers<sup>9,27-30</sup> has then been used to calculate the limiting low pressure rate constants  $k_{10}^{sc}$ , and subsequently, the values for  $k_1(T,P)$ . The calculation closely follows that of Kondo *et al.*,<sup>26</sup> except that the JANAF<sup>17</sup> values for CH<sub>3</sub>Cl vibration frequencies along with the Whitten-Rabinovitch formulas<sup>37</sup> have been used for vibrational state density determination. We have also used ( $\sigma_{\text{CH}_3\text{Cl},\text{Ar}}$ ,  $\epsilon_{\text{CH}_3\text{Cl},\text{Ar}}/k$ ) values of (3.78 Å, 205.5 K) along with tabulated integrals for  $Z_{IJ}$  determination.<sup>33</sup> The results for the various parametric quantities that are used in the calculation are given in Table III. Comparison of these values with corresponding values from Kondo et al.<sup>26</sup> shows good agreement, and therefore, the presently derived  $k_{10}^{sc}$  values are likewise in good agreement being ~60% of those of Kondo *et al.*<sup>26</sup> The above values for both  $k_{1\infty}$  and  $k_{10}^{sc}$ , along with the LJ model for the transition state and assumed values for the collisional deactivation efficiency factor  $\beta_c$ , can then be used to calculate values for  $S_K$ ,  $B_K$ ,  $F_{cent}$ , and finally,  $k_1(T,P) = k_{1\infty}F_{LH}F(P_r)$ , where  $F_{LH}$  is the Lindemann-Hinshelwood factor

 $P_r/(1+P_r)$ , and  $F(P_r)$  is the broadening factor, a function of reduced pressure  $P_r = \beta_c k_{10}^{sc}(M)/k_{1\infty}^{.9,27-30}$  The final results are fitted to the data of Fig. 5 with the fitting parameter being  $\Delta E_{\rm down}$ , which in turn determines  $\beta_c$ . We find that values of  $\Delta E_{\rm down}$  between 1400 and 1800 cm<sup>-1</sup> can adequately explain the data. Figure 8 compares the theoretical predictions with  $\Delta E_{\rm down} = 1600$  cm<sup>-1</sup> to the data from the three loading pressures. The previously noted slight pressure dependence is fairly well corroborated. The theoretically predicted spread between the 6 and 15 Torr sets  $\pm 32\%$  is negligibly higher than the experimental spread  $\pm 29\%$ . Also, the predicted activation energy is 67.5 in contrast to the measured value from Eq. (3) of  $(55.3\pm3.1)$  kcal mol<sup>-1</sup>, and the predicted A factor is about 30 times larger than measured. These differences are

10<sup>5</sup>  $CH_3CI \rightarrow CH_3 + CI$ 10<sup>4</sup>  $10^{3}$ 15 Torr 10<sup>2</sup> **10**<sup>4</sup> k /s<sup>-1</sup> 10<sup>3</sup> 10 Torr 10<sup>2</sup>  $10^{4}$ 10<sup>3</sup> 6 Torr  $10^2$ 6 7 5 10000 K/T

FIG. 8. A comparison of the experimental data and the theoretical calculation for  $k_1(T,P)$ . The data points are the same as those in Fig. 5. The calculated lines are from the semiempirical form of Troe theory for unimolecular reactions (see the text).

undoubtedly due to data scatter and the small range of the data base in  $T^{-1}$  in a linear least-squares analysis with the equation,  $\log k = \log A - B/T$ . The final values of additional quantities are also given in Table III along with the derived value of  $\beta_c$  from  $\Delta E_{\text{down}} = 1600 \text{ cm}^{-1}$ .

The theoretical calculations of Kondo et al.<sup>26</sup> are nearly the same as the present. Therefore, as anticipated, the large difference in the experimental results from the two studies is reflected in the respective values of  $\Delta E_{\text{down}}$ , with the present value being  $1600 \text{ cm}^{-1}$  in contrast to  $\sim$  310 cm<sup>-1</sup> obtained in their work. The question as to whether the present results are reasonable then rests on the plausibility of the derived value for  $\Delta E_{\text{down}}$ . Admittedly, the magnitude of this value is higher than in other thermal decompositions, with usual values ranging from  $\sim 400$  to  $800 \text{ cm}^{-1}$  (Ref. 38); however, it should be noted that a similarly high value is necessary to explain the thermal decomposition of CCl<sub>4</sub>.<sup>39</sup> If  $\Delta E_{down}$  has physical significance, then the present value would suggest a very efficient energy transfer from vibrational degrees of freedom in excited CH<sub>3</sub>Cl to translation in Ar. This in turn might suggest that the dominant effect in this case (and in  $CCl_4$ ) is a mass effect; i.e., the probability of energy transfer is large because the masses of Cl and Ar are nearly the same. Such a classical explanation has been discussed in detail.<sup>40</sup> Lastly, the necessarily large value of  $\Delta E_{\text{down}}$  might also be a consequence of inadequacies in the semiempirical form of Troe theory for this type of thermal decomposition.

# O+CH<sub>3</sub>→products

Some general points can be made from a comparison of the simulations shown in Figs. 3 and 7.  $[CH_3]_t$  is lowered by the presence of O atoms even though the levels of HCl, CH<sub>2</sub>Cl, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub> formation remain about the same. Only  $[H]_t$  and  $[H_2CO]_t$  change drastically. The cause for the decrease in  $[CH_3]_t$  and the increases in  $[H]_t$  and  $[H_2CO]_t$  is clearly reaction (2). Also in the simulation, we have assumed that the products of reaction (2) are H and H<sub>2</sub>CO, even though there is recent evidence at 298 K that the product yields may be more complex. Seakins and Leone<sup>41</sup> have claimed that both  $H_2CO+H$  and  $H_2+CO+H$ are products with the branching ratios being 0.6 and 0.4, respectively, at room temperature. The present experiments cannot confirm these findings; however, if the branching ratio to the latter product set is as high as claimed, then even higher values might be expected at the temperatures of the present experiments. If this were true, then it might have a significant impact on the chemical modeling of methane oxidation.

Figure 7 shows the temporal profile of CH<sub>3</sub> radicals and O atoms. Since CH<sub>3</sub>Cl decomposition is still contributing to [CH<sub>3</sub>]<sub>t</sub> in the early stages of reaction, a pseudofirst-order analysis would approximately hold because the average [CH<sub>3</sub>] [i.e.,  $\langle$ CH<sub>3</sub> $\rangle$ , the time weighted integral of [CH<sub>3</sub>]<sub>t</sub>] would be  $\sim 8 \times 10^{12}$  molecules cm<sup>-3</sup>. As mentioned above, the pseudo-first-order rate constant is (1465  $\pm 165$ ) s<sup>-1</sup>, and this then gives  $k_2 \approx 1.8 \times 10^{-10}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The effects of the random error in  $k_1(\pm 29\%)$  has been examined by applying correlation analysis<sup>42</sup> to the mechanism of Table I. This level of uncertainty can cause a  $\sim \pm 7\%$  uncertainty in the derived values of  $k_2$ . Also, the effects of the CH<sub>3</sub> radical chemistry have been evaluated with correlation analysis<sup>42</sup> and, as might be anticipated because so little secondary products are formed, this analysis shows that uncertainties in the CH<sub>3</sub> radical chemistry [reactions (4), (5), and (7) in Table I] contribute only 0.1% uncertainty to the value for  $k_2$ . Hence, this source of error is negligible. The general conclusion is that the rate constant can be obtained under nearly isolated conditions, and therefore, the determination is quite direct.

The 15 determinations in Table II give  $k_2 = 1.4 \times 10^{-10}$  $cm^3$  molecule<sup>-1</sup> s<sup>-1</sup> with a  $\pm 20\%$  error from repeat determinations; however, this is not the absolute error since there are systematic errors inherent in the determinations. For example, there is a systematic error in the choice of a best profile for a given experiment with the effect being  $\sim \pm 10\%$  of the chosen  $k_2$ , but this is already included the Table II error analysis. There is one other systematic error that this is not included. Even though  $[O]_0$  is fitted to a particular profile from a knowledge of an extrapolated value for (ABS)<sub>0</sub> and  $\sigma_{O \text{ atom}} l$ , it is really known absolutely to  $\sim \pm 20\%$  as mentioned in the experimental section. With this level of uncertainty, the mechanism of Table I has again been used to simulate experiments. This amounts to rescaling the experiments by attributing all of the error to the scale factor  $\sigma_{O atom}l$ . The final values for  $k_2$  can change by  $\sim \pm 10\%$  due to this effect. This is consistent with the derived values for  $\langle CH_3 \rangle$  from the simulated experiments. The  $\pm 20\%$  variation in  $[O]_0$  yields a  $\sim \pm 10\%$ variation in the time weighted average. Combining all random and systematic errors, we believe that the present determination is absolutely accurate to  $\sim \pm 35\%$ . Our value  $k_2 = 1.4 \times 10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> com-

Our value  $k_2=1.4\times10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> compares quite favorably to lower temperature direct data. Washida and Bayes<sup>43</sup> have reported  $k_2=(1.0\pm0.2)$  $\times10^{-10}$  between 259 and 341 K; Plumb and Ryan<sup>44</sup> have measured a room temperature value of  $(1.1\pm0.3)\times10^{-10}$ ; and, in the most extensive lower temperature study, Slagle, Sarzynski, and Gutman<sup>45</sup> have determined  $k_2=(1.4\pm0.2)$  $\times10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> between 294 and 900 K. The high temperature shock tube result between 1600 and 2400 K of Bhaskaran, Frank, and Just<sup>46</sup>  $k_2=1.4\times10^{-10}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> is also in excellent agreement with the present value. Therefore,  $k_2$  appears to be invariant within experimental error from 259 to 2400 K at  $(1.3\pm0.2)$  $\times10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.

A theoretical value for the reaction (2) rate constant can be estimated from a LJ expression that is similar to Eq. (5). Here,  $g^{\ddagger}=4$  because the transition state correlates with CH<sub>3</sub>O, where the Jahn-Teller distortion from the <sup>2</sup>E state is small, and the resulting <sup>2</sup>A' and <sup>2</sup>A'' states are nearly degenerate<sup>47</sup> with a splitting energy of only 0.12 kcal mol<sup>-1</sup>. Also,  $g_{CH_3} = 2$ , and  $g_0=5+3 \exp(-228/T)$  $+\exp(-326/T)$  in the calculation. From diffusion coefficient data,<sup>48</sup> ( $\sigma,\epsilon/k$ ) values for O atoms can be derived; i.e., (2.92 Å, 80.9 K). Combining these with those for CH<sub>3</sub>



FIG. 9. An experimental profile of [H], at reaction conditions T=1614 K, P=510 Torr,  $\rho=3.048\times10^{18}$ , [CH<sub>3</sub>Cl]= $2.493\times10^{13}$ , [SO<sub>2</sub>]= $1.519\times10^{14}$ , and [O]<sub>0</sub>= $4.00\times10^{12}$  molecules cm<sup>-3</sup>. The dashed line is the simulated [H], profile from the reactions in Table I for the decomposition of CH<sub>3</sub>Cl without O atoms. The solid line is the simulated [H], including reactions (2) and (9) of Table I, the best fit being with  $k_2=1.1\times10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. The experiment shows unambiguously that H atoms are a product from the reaction of O+CH<sub>3</sub>.

and evaluating Eq. (5) for the O+CH<sub>3</sub> reaction gives a nearly temperature invariant value between 300 and 2500 K of  $(1.44\pm0.13)\times10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. This agrees with the experimental result, but this type of model may be too simplified since it does not take into account specific state correlations. This simple estimate does suggest that the reaction occurs at the collision rate, probably with no recrossing. The flexible transition state theory method<sup>31,32</sup> is currently being applied to the present and several other cases where the potential energy surfaces are being determined by *ab initio* methods.<sup>49</sup> These results will be compared to those from the presently described LJ method.

Lastly, five experiments were performed in the absence of SO<sub>2</sub>, in which H atoms were quantitatively observed. From these limited data, the value for  $k_5$  in Table I was inferred. Even though this value does not agree with a more recent determination,<sup>50</sup> the disagreement is probably due to the limited data set and perhaps the neglect of other H atom producing processes. The listed  $k_5$  value does at least give an empirical description of the level of [H] formed as a function of temperature without O atoms. Experiments were then performed with O atoms being present in order to see if the rate of formation of H atoms does increase because of reaction (2). Figure 9 shows a typical result at 1614 K. A simulation of the experiment without O atoms gives the predicted H-atom profile shown as the dashed line where the H-atom yield would be  $\sim 2.7 \times 10^{11}$ molecules cm<sup>-3</sup> at 1.2 ms. In contrast, for  $[O]_0=4\times10^{12}$ molecules cm<sup>-3</sup>, the predicted profile is given by the solid line with  $k_2=1.1\times10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. There is only fair agreement between prediction and measurement, but the experiment shows unambiguously that H atoms are

released by photolysis, and the large enhancement in yield is undoubtedly due to reaction (2). Hence, H atoms are a product of reaction (2), but these limited experiments cannot distinguish between the other products suggested by Seakins and Leone,<sup>41</sup> namely, H<sub>2</sub>CO or H<sub>2</sub>+CO.

# ACKNOWLEDGMENTS

The authors wish to thank Dr. L. B. Harding and Dr. A. F. Wagner for a thorough reading of the manuscript and helpful suggestions. We also especially thank Dr. J. P. Hessler for critically reading the manuscript and for performing the correlation analysis with the Table I mechanism. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under Contract No. W-31-109-Eng-38.

- <sup>1</sup>B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases*, 3rd ed. (Academic, Orlando, 1987). See also the original edition (1938) and the 1st and 2nd editions (1952 and 1962), respectively.
- <sup>2</sup>F. S. Dainton, *Chain Reactions* (Methuen, London, 1966).
- <sup>3</sup>J. N. Bradley, *Flame and Combustion Phenomena* (Methuen, London, 1969).
- <sup>4</sup>H. Gg. Wagner, Symp. (Int.) Combust. (Proc.) 14, 27 (1972).
- <sup>5</sup>S. C. Khandelwal and G. B. Skinner, *Shock Waves in Chemistry*, edited by A. Lifshitz (Dekker, New York, 1981).
- <sup>6</sup>J. D. Bittner and J. B. Howard, Symp. (Int.) Combust. (Proc.) **19**, 211 (1982).
- <sup>7</sup>C. K. Westbrook and F. L. Dryer, Prog. Energy Combust. Sci. 10, 1 (1984) and references therein.
- <sup>8</sup>J. A. Miller and C. T. Bowman, Prog. Energy Combust. Sci. 15, 287 (1989).
- <sup>9</sup> R. J. Kee, F. M. Rupley, and J. A. Miller, Sandia Report No. SAND89-8009, UC-401, September, 1989.
- <sup>10</sup> R. J. Kee, F. M. Rupley, and J. A. Miller, Sandia Report No. SAND87-8215B, UC-4, March, 1990.
- <sup>11</sup>A. E. Lutz, R. J. Kee, and J. A. Miller, Sandia Report No. SAND87-8248B, UC-401, July, 1990.
- <sup>12</sup>W. Tsang and A. Lifshitz, Annu. Rev. Phys. Chem. 41, 559 (1990).
- <sup>13</sup>A. Fontijn and R. Zellner, in *Reactions of Small Transient Species*. *Kinetics and Energetics*, edited by A. Fontijn and M. A. A. Clyne (Academic, London, 1983), p. 1.
- <sup>14</sup>J. V. Michael, Prog. Energy Combust. Sci. 18, 327 (1992) and references cited therein.
- <sup>15</sup>D. A. Whytock, J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, J. Chem. Phys. **66**, 2690 (1977).
- <sup>16</sup> M. A. A. Clyne and W. S. Nip, J. Chem. Soc. Faraday Trans. 2 72, 838 (1976).
- <sup>17</sup> M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Chem. Ref. Data 14, Supplement No. 1 (1985).
- <sup>18</sup>W. B. DeMore, S. P. Sander, D. M. Golden, M. J. Molina, R. F. Hampson, M. J. Kurylo, C. J. Howard, and A. R. Ravishankara, Evaluation No. 9, JPL Publication 90-1, January 1, 1990.
- <sup>19</sup> D. Walter, H.-H. Grotheer, J. W. Davies, M. J. Pilling, and A. F. Wagner, Symp. (Int.) Combust. (Proc.) 23, 107 (1990).
- <sup>20</sup>Y. Feng, J. T. Niiranen, A. Bencsura, V. D. Knyazev, D. Gutman, and W. Tsang, J. Phys. Chem. (in press).
- <sup>21</sup>R. D. Kern, H. J. Singh, and C. H. Wu, Int. J. Chem. Kinet. 20, 731 (1988).
- <sup>22</sup>T. Ko, A. Fontijn, K. P. Lim, and J. V. Michael, Symp. (Int.) Combust. (Proc.) 24, (in press).
- <sup>23</sup>J. V. Michael and A. F. Wagner, J. Phys. Chem. 94, 2453 (1990).
- <sup>24</sup>J. V. Michael and K. P. Lim, J. Chem. Phys. 97, 3228 (1992).
- <sup>25</sup>J. H. Lee, J. V. Michael, W. A. Payne, and L. J. Stief, J. Chem. Phys. 69, 3069 (1978).
- <sup>26</sup>O. Kondo, K. Saito, and I. Murakami, Bull. Chem. Soc. Jpn. 53, 2133 (1980).
- <sup>27</sup>J. Troe, J. Chem. Phys. 65, 4745 (1977); 65, 4758 (1977).
- <sup>28</sup>J. Troe, J. Phys. Chem. 83, 114 (1979).
- <sup>29</sup>J. Troe, Ber. Bunsenges. Phys. Chem. 87, 161 (1983).

<sup>30</sup>R. G. Gilbert, K. Luther, and J. Troe, Ber. Bunsenges. Phys. Chem. 87, 169 (1983).

- <sup>31</sup>D. M. Wardlaw and R. A. Marcus, Chem. Phys. Lett. 110, 230 (1984);
   J. Chem. Phys. 83, 3462 (1985).
- <sup>32</sup> W. L. Hase, S. L. Mondro, R. J. Duchovic, and D. M. Hirst, J. Am. Chem. Soc. **109**, 2916 (1987).
- <sup>33</sup> J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1966).
- <sup>34</sup> J. V. Michael, D. F. Nava, W. A. Payne, and L. J. Stief, J. Chem. Phys. 70, 1147 (1979).
- <sup>35</sup>H. S. Judeikis and M. Wun, J. Chem. Phys. 68, 4123 (1978).
- <sup>36</sup> M. Weissman and S. W. Benson, Int. J. Chem. Kinet. 16, 307 (1984).
   <sup>37</sup> G. Z. Whitten and B. S. Rabinovitch, J. Chem. Phys. 38, 2466 (1963); 41, 1883 (1964).
- <sup>38</sup>W. Tsang, Combust. Flame 78, 71 (1989).
- <sup>39</sup>J. V. Michael, K. P. Lim, S. S. Kumaran, and J. H. Kiefer, J. Phys. Chem. (in press).
- <sup>40</sup>S. W. Benson, *The Foundations of Chemical Kinetics* (McGraw-Hill, New York, 1960), p. 161.

- <sup>41</sup> P. W. Seakins and S. R. Leone, J. Phys. Chem. 96, 4478 (1992).
- <sup>42</sup>The method is described in J. P. Hessler and P. J. Ogren, J. Chem. Phys. 97, 6249 (1992).
- <sup>43</sup>N. Washida and K. D. Bayes, Int. J. Chem. Kinet. 8, 777 (1976).
- 44 I. C. Plumb and K. R. Ryan, Int. J. Chem. Kinet. 14, 861 (1982).
- <sup>45</sup>I. R. Slagle, D. Sarzynski, and D. Gutman, J. Phys. Chem. **91**, 4375 (1987).
- <sup>46</sup>K. A. Bhaskaran, P. Frank, and Th. Just, *Proceedings of the 12th International Symposium on Shock Tubes and Waves*, edited by A. Lifshitz and J. Rom (Magnes, Jerusalem, 1980), p. 503.
- <sup>47</sup>S. Saebø, L. Radom, and H. F. Schaefer III, J. Chem. Phys. 78, 845 (1983).
- <sup>48</sup> I. C. Plumb, K. R. Ryan, and N. G. Barton, Int. J. Chem. Kinet. 15, 1081 (1983).
- <sup>49</sup>A. F. Wagner, L. B. Harding, and J. V. Michael (in preparation).
- <sup>50</sup> P. Frank and M. Braun-Unkhoff, Shock Tubes and Waves, Proceedings of the 16th International Symposium on Shock Tubes and Waves (VCH, New York, 1988), p. 379.