

Pressure Dependence of the Rate Constants for the Reactions $\text{CH}_3 + \text{O}_2$ and $\text{CH}_3 + \text{NO}$ from 3 to 10^4 Torr

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A relative rate technique is used to measure the pressure dependence of the rate constants for reaction 1 ($\text{CH}_3 + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{M}$) and reaction 3 ($\text{CH}_3 + \text{NO} + \text{M} \rightarrow \text{CH}_3\text{NO} + \text{M}$) relative to reaction 2 ($\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} + \text{Cl}$). The pressure dependence of the rate constant of reaction 3 at 297 K can be represented in the Troe equation by the parameters $(k_3)_0 = (3.5 \pm 0.4) \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, $(k_3)_\infty = (1.68 \pm 0.1) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $F_{\text{cent}} = 0.46$. The values of k_3 are identical to those observed in recent absolute rate measurements at 296 K and 27–600 Torr, verifying that the rate constant chosen for reaction 2, $k_2 = 3.95 \times 10^{-12} \exp(-530/RT)$, is both pressure independent and correct at 296 K. This value of k_2 was used to determine absolute values of k_1 from the ratio k_1/k_2 in N_2 diluent for pressures between 3 and 11 000 Torr at 297 K, between 20 and 1500 Torr at 370 K, and between 40 and 1500 Torr at 264 K. All data in N_2 can be fitted using the following parameters in the Troe equation: $(k_1)_0 = (7.56 \pm 1.1) \times 10^{-31} (T/300)^{-3.64 \pm 1.0} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$; $(k_1)_\infty = (1.31 \pm 0.1) \times 10^{-12} (T/300)^{1.2 \pm 0.8} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; $F_{\text{cent}} = 0.48$ (264 K), 0.46 (297 K), 0.42 (370 K). Error limits include statistical error and the uncertainty in k_2 . In He, N_2 , and SF_6 diluents the relative third-body efficiencies are 0.56:1.0:1.52, respectively, assuming that F_{cent} is independent of diluent. The high-pressure limit in SF_6 is identical to that in N_2 . Rate constant ratios were also measured at 297 K for $\text{CD}_3 + \text{O}_2 + \text{M} \rightarrow \text{CD}_3\text{O}_2 + \text{M}$ (1D) between 5 and 6000 Torr. Assuming that $k_{2D} = k_2$, the limiting rate constants using $F_{\text{cent}} = 0.46$ are $(k_{1D})_0 = (11.8 \pm 1.6) \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ and $(k_{1D})_\infty = (1.38 \pm 0.08) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

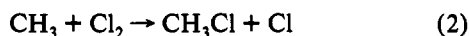
Introduction

The addition reaction of O_2 to CH_3 is important in both combustion and atmospheric oxidation. Because it is the simplest example of the addition of oxygen to an alkyl radical, it has been studied in detail, as summarized in the most recent experimental publication on the topic.¹ However, the agreement between the experiments is somewhat less than desirable as exemplified by the factor of 2 discrepancy in the determination of $(k_1)_\infty$



A value of $(k_1)_\infty = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained from data at pressures below 1 atm by Keiffer et al.¹ while Cobos et al.² determined the high-pressure rate constant to be $2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in studies at pressures up to 100 atm.

This paper uses a relative rate technique to examine reaction 1 in N_2 at pressures from 3 to 10^4 Torr (covering both the predominantly high- and low-pressure regions) and at temperatures from 264 to 370 K. In addition, three other diluents were studied at 297 K (He, Ar, and SF_6) in order to explore the third-body efficiency of these species and to enable comparison with rate constants presented in other publications. The pressure dependence of the rate constant of reaction 1 was measured relative to the rate constant of reaction 2



The absolute rate constant of reaction 2 has been determined in two experiments,^{3,4} both of which were carried out at low pressure (2–12 Torr). The values obtained in these measurements at 297 K were $k_2 = (1.54 \pm 0.11) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from data in Table I of ref 3 and $(1.81 \pm 0.36) \times 10^{-12}$ from the temperature dependence plot in Figure 2 of ref 4. Combining these two measurements using a weighted average in which the weighting factors are the inverse of the stated error limits gives a value for $k_2 = (1.61 \pm 0.1) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value was used

to place the relative rate constants measured for k_1 on an absolute basis at 297 K. The temperature dependence of k_2 was assumed equal to that measured by Timonen and Gutman⁴ ($E_a = 530 \pm 125 \text{ cal/mol}$).

Although reaction 2 is expected to be pressure independent and shows no pressure dependence between 2 and 12 Torr, this fact needs to be verified prior to use of this reaction as a reference at much higher pressures. To provide such verification and to check the absolute value of k_2 used to determine k_1 from the relative rate data at 297 K, the rate constant of reaction 3



was also measured relative to that of reaction 2. The values of k_3 obtained from this relative rate study were then compared to the absolute values of k_3 measured by Davies et al.⁵ at pressures from 27 to 600 Torr in Ar.

For both studies, the reaction was initiated by UV irradiation of mixtures containing Cl_2 , CH_4 , a diluent, and either O_2 or NO . In the following sections, we will first discuss the relative rate determination of k_3 and then present the determination of the rate constant k_1 . In the process, the current results will be compared to the other measurements of k_1 in the four bath gases, and they will also be used to obtain values of $(k_1)_0$ and $(k_1)_\infty$ as functions of temperature.

Experiment

Two reactors were used in these experiments. At pressures below 2 atm, measurements were made in a 0.2-L Pyrex reactor (5-cm i.d.) equipped with a temperature-controlling jacket, which has been described in detail elsewhere.⁶ The temperature was maintained to $\pm 2 \text{ K}$ by circulating an ethylene glycol-water mixture through the jacket using a constant-temperature recirculator. For pressures from 1 to 15 atm, a cylindrical 0.05-L (3.7-cm i.d. \times 4.5-cm-long) stainless steel pressure reactor equipped with $3/4$ -in.-thick quartz windows on each end was employed.

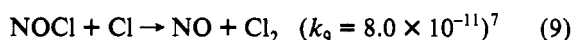
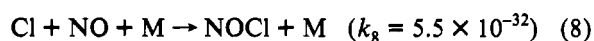
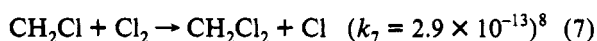
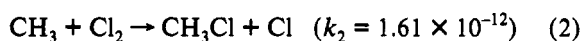
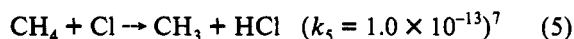
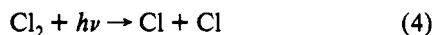
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Premixed reactants containing CH₄, Cl₂, diluent (N₂, Ar, He, or SF₆), and O₂ or NO were introduced into one of the reactors. The reactor was irradiated by a Sylvania black-light-blue fluorescent lamp for a fixed period of time, after which the contents of the reactor were removed into a 500-cm³ Pyrex storage flask and analyzed by gas chromatography (GC) for methane and methyl chloride. Thus, each irradiation of a mixture produced a single data point. By comparing the methane concentration in the unreacted mixture to that present after irradiation, the percentage consumption of CH₄ was determined to an accuracy better than 0.5% of the initial CH₄ concentration. The concentration of CH₃Cl was determined by calibration of the GC response using standard mixtures.

The Cl₂ (Matheson, 99.99%) and NO (Matheson, 99%) were degassed prior to use by freezing at liquid nitrogen temperature. CH₄ (Airco, 99.995%), He (Matheson, 99.999%), O₂ (Matheson, 99.995%), Ar (Matheson, 99.998%), and N₂ (Airco, 99.999%) were used as purchased. Reaction mixtures were prepared by placing known pressures of the reactants either into a 1-L Pyrex storage flask for the lower pressure tests or into 1- or 3.8-L steel pressure vessels for high-pressure experiments. These mixtures were allowed to mix for several hours prior to initial use.

Results

A. CH₃ + NO Reaction. In the relative rate study of reaction 3, mixtures of CH₄, Cl₂, NO, and Ar were used. After irradiation at 297 K in one of the reactors, the contents of the reactor were analyzed for CH₄ and CH₃Cl. The measured [ΔCH₄] and [CH₃-Cl] were then fitted by varying the value of *k*₃ in a computer simulation of the following mechanism (bimolecular rate constants, cm³ molecule⁻¹ s⁻¹; termolecular, cm⁶ molecule⁻² s⁻¹):

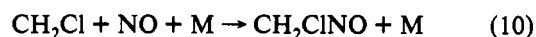


The rate of eq 4, which depends on the photon flux, was adjusted to obtain the correct CH₄ decay rate. However, this was done only for aesthetic reasons. Because this is a relative rate study in which only ΔCH₄ and CH₃Cl need to be fit, the absolute rate of CH₄ consumption, and, therefore, the Cl atom concentration does not affect the calculated rate constant ratio at all. In these mixtures, reaction 8 is fast relative to reaction 5, and it might appear that measurement of *k*₃ would be impossible because the Cl would react primarily with NO, removing Cl₂ and NO. However, reaction 9 is fast, and a photostationary state is established in which the steady-state NOCl density is low. Thus, net consumption of Cl₂ and NO by reaction 8 is small. This fact also assures that any NOCl formed in the dark during mixture storage will be rapidly converted back to NO and Cl₂ immediately after the irradiation begins and before appreciable CH₄ consumption takes place.

Reactions 8 and 9 do not affect the fitted value of *k*₃ in these experiments until very high pressures are reached where the

steady-state NOCl density is larger. The value of *k*₈ presented above is determined by combining the recommended value⁷ in N₂ with the measured efficiency of Ar relative to N₂ at the low-pressure limit.⁹ This value was used for pressures below 1 atm. For higher pressures, the high-pressure limiting rate constant (= 3 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹) was set equal to that of the analogous reaction O + NO = NO₂.¹⁰ *k*₈ was then estimated from the Troe equation¹¹ using the center broadening factor for reaction 8 suggested by Patrick and Golden¹² (*F*_{cent} = 0.74). At 10 atm, the value of *k*₈ was a factor of 2 smaller than that calculated from the low-pressure limiting rate constant. Decreasing the value of *k*₈ by a factor of 2 decreases the calculated value of *k*₃ by only 4% at this pressure. For pressures below 3 atm, the Troe calculation of *k*₃ produces a negligible change in *k*₃, and therefore, uncertainty in *k*₈ does not affect the measured value of *k*₃ to within experimental error. The primary effect of reactions 8 and 9 is to control the steady-state Cl atom concentration and, therefore, the overall rate of CH₄ consumption.

Reaction 6 is very important to the determination of *k*₃ because this secondary consumption reaction is 5 times faster than that of reaction 5. However, the ratio *k*₆/*k*₅ (=4.8) is well established,^{10,13} and the correction can be made accurately. Another reaction might play a role in the reacting mixture



although its rate constant is unknown. Adding this reaction to the mechanism with a rate constant equal to *k*₃ changes the calculated value of *k*₃ by less than 1% for our experimental conditions. The fit is very insensitive to the values chosen for reactions 7 and 10 because the effect of these reactions is only to change the concentrations of NO and Cl₂ slightly as the reaction progresses. These reactants are in considerable excess over the methyl chloride consumed by reaction with Cl, and no systematic change in rate constant ratio is observed as the percentage consumption of CH₄ increases.

One additional uncertainty occurred during the measurements in which high-pressure mixtures were stored in the 1-L steel, high-pressure, storage vessel. When a mixture was stored in the Pyrex vessel, values of *k*₃ obtained at the same reactor pressure were identical over a period of 3 days, indicating that the mixture composition remained constant. In contrast, the measured value of *k*₃ increased by approximately 10–15%/day when a mixture was stored in the high-pressure vessel. The initial measurements performed within 18 h of mixing averaged approximately 7% higher than those from mixtures stored in the Pyrex vessel. This suggests that a component in the unreacted mixture, probably NOCl formed by the slow reaction of Cl₂ with NO, reacts with the metal storage vessel. Loss of NOCl in these mixtures would increase the Cl₂/NO ratio, thereby increasing the apparent value of *k*₃, because 1 NO and 1/2 Cl₂ would be lost per NOCl. In addition, the Cl₂/NO ratio in the mixtures stored in the steel vessel was always greater than 2, which accentuates the effect of loss of NOCl on this ratio. Cotton and Wilkinson¹⁴ note that NOCl is a powerful oxidant and reacts rapidly with many metals. Thus, NOCl loss might be expected to occur. Because of the change in composition of the high-pressure mixtures with storage time, the values of *k*₃ determined at high pressure were scaled by the ratio *k*₃(glass storage vessel)/*k*₃(steel storage vessel) at 560 Torr. The scaling factor, which varied from 0.8 to 1 depending upon the storage time of the mixture in the steel vessel, was determined concurrently with the high-pressure measurements each day.

Eleven separate mixtures were tested in these experiments over the pressure range 27–7600 Torr. Because reaction 3 is pressure dependent, causing the optimum reactant concentrations to vary, not all mixtures were used over the entire pressure range. The most extensive test of mixture composition was carried out at 560 Torr. Table I presents all data obtained at 560 Torr in both

TABLE I: Determination of k_3 at 560 or 5625 Torr with Ar Diluent

(CH ₄) ₀ (ppm)	(NO) ₀ (ppm)	(Cl ₂) ₀ (ppm)	ΔCH ₄ ^a (ppm)	CH ₃ Cl ^b (ppm)	time ^c (min)	k_3^d (×10 ¹²)
875 ^e	1563	7815	67	29.4	5	7.05
			147	49.5	15	7.6
			237	60.1	30	7.9
889 ^e	3556	890	68	9.0	28	6.7
			130	13.5	70	7.2
			76	35.2	6	6.4
951 ^e	1698	8490	159	56.1	15	7.0
			238	67.7	30	6.9
			174	58.3	15	7.5
969 ^e	1700	8500	200	63.4	15	7.5
975 ^e	1700	8500	87	4.6	25	6.37
2643 ^e	11010	2753	235	10.6	90	6.37
			153	7.9	60	6.65
2642 ^e	11010	2970	264	11.8	120	6.95
			235 ^f	11.3	116	6.6
			252	12.1	120	6.4
2472 ^e	10300	2781	3.6 ^h	1.27	7.5	7.8
33 ^e	203	879	4.4 ⁱ	1.46	17	7.8
			12.4 ^h	2.06	30	7.6
			1.7 ^j	0.54	25	12.9
			4.1 ^j	1.00	59	14.7
			13.2 ^j	1.35	265	17.1

^a Amount of CH₄ consumed during the irradiation. ^b Mole fraction of CH₃Cl formed. ^c Irradiation time. ^d Calculated rate constant (cm³ molecule⁻¹ s⁻¹). ^e Each entry showing a new set of initial reactant concentrations represents a new mixture. Data sets with no initial concentrations specified are multiple determinations of k_3 using the mixture specification on a line above the entry. The total pressure is 560 Torr; jacketed-Pyrex reactor is used. Mixture stored in Pyrex vessel. ^f Experiment run after 2 days of mixture storage in the Pyrex storage vessel. ^g Mixture stored in 1-L steel vessel. ^h Pyrex reactor at 560 Torr. ⁱ 0.05-L steel reactor at 560 Torr. ^j 0.05-L steel reactor at 5625 Torr. The value of k_3 is unscaled. The true value is obtained by multiplying the tabulated value by the scaling factor of 0.89 (see text, section A).

reactors and at 5625 Torr in the steel reactor. In this table, each new methane entry represents a separate initial mixture. The measured value of k_3 at 560 Torr in the glass reactor is independent of the percentage of the initial methane consumed (3.3–27%), the Cl₂/NO ratio (0.25–5), and the Cl₂/CH₄ ratio (1–9). This provides substantial verification of the mechanism used to evaluate k_3 (see discussion of mechanism verification for k_1 in the Appendix). Also included in this table is a data set obtained from a single mixture at both 560 and 5625 Torr using the steel storage vessel. The data at 560 Torr from this mixture were combined with the average of the k_3 values from the glass storage vessel at 560 Torr ($=6.95 \times 10^{-12}$) to obtain the scaling factor ($=0.89$). This factor was used to determine the true value of k_3 for the experiments at 5625 Torr as described above. The high-pressure data in Table I span a factor of 8 (5–40%) in percentage consumption of methane; the scatter in the rate constant ratio is within the experimental error even for this wide range of consumption. As presented in the table, experiments using the high-pressure mixture were carried out at 560 Torr in both the Pyrex and the steel reactors. The results for these vessels are indistinguishable, providing evidence that the rate constant ratios are not affected by surface reactions.

Additional experiments were carried out at pressures between 27 and 7600 Torr, during which the percentage of CH₄ consumption and the mixture composition were varied over smaller ranges. Again, no change in k_3 was observed when these experimental variables were altered. All pressure-dependent data are presented in Figure 1. Although no significant effect of methane consumption on the rate constant ratios was noted, the few points with very high CH₄ consumption (>29%) were not included in the figure or in the final data fits. Because 16 points were obtained at 560 Torr and 13 at 27 Torr, only the average at these two pressures is plotted along with their standard deviations (2σ of the mean) for clarity of presentation. All of the

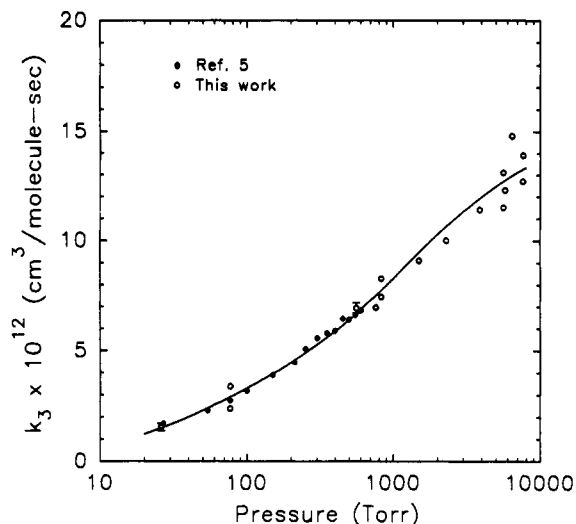


Figure 1. Measured values of k_3 determined in Ar diluent by the relative rate technique compared to those obtained in absolute measurements by Davies et al.⁵ at 297 K. The solid line represents a Troe fit to the relative rate data using constants presented in the text. Data points at 27 and 560 Torr are averages of 13 and 16 experiments with 2σ statistical errors of 13 and 4%, respectively. All other points represent single determinations.

data have been fitted to a Troe expression¹¹ using the center broadening factor ($=0.46$) calculated by Patrick and Golden¹² for reaction 1. The solid line in Figure 1 represents this falloff curve [$(k_3)_0 = (3.5 \pm 0.4) \times 10^{-30}$ cm⁶ molecule⁻² s⁻¹; $(k_3)_\infty = (1.68 \pm 0.1) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹]. The quoted error limits are 2σ statistical uncertainties in the fit (see section B).

Also plotted in Figure 1 are the absolute rate constants obtained by Davies et al.⁵ for reaction 3. As is evident, the values of k_3 measured in the current experiment agree exactly with the absolute data of Davies et al. over the range of their measurements. These results provide verification that there is no pressure dependence to reference reaction 2 over the range 27–600 Torr. In addition, the value of k_2 used to obtain absolute constants from these relative rate measurements is perfectly consistent with the data of Davies et al. This provides strong support for the absolute value of k_2 which will be used to obtain absolute values of k_1 in the following section.

B. CH₃ + O₂ Reaction. Experiments similar to those described above were performed to measure the rate constant ratio k_1/k_2 . In these experiments, mixtures of CH₄, O₂, Cl₂, and M (N₂, He, Ar, SF₆) were placed into the 3.8-L steel storage vessel. For these mixtures, no reactions occurred in this storage vessel over periods of days as demonstrated by the fact that the rate constant ratios did not change and no CH₃Cl formation occurred during storage. Unreacted mixtures were added to one of the reactors and were irradiated for a chosen time. The contents of the reactor were then removed and analyzed for CH₄ loss and CH₃Cl formation. Data were obtained in N₂ (or O₂) diluent over the pressure range 3–10⁴ Torr at 297 K, 20–1500 Torr at 370 K, and 40–1100 Torr at 264 K. At 297 K, experiments were also performed between 8 and 8000 Torr in SF₆. For He (8–300 Torr) and Ar (50–500 Torr) diluents, more limited pressure ranges were examined at 297 K, primarily for comparison to data in other publications.

The data were fitted by computer integration of a mechanism consisting of reactions 1 (irreversible at 297 K), 2, 4, 5, 6, 7, and 11:



As with the analogous NO reaction, the rate constant of reaction 11 is unknown and was set equal to that of reaction 1 at each pressure. Inclusion of this reaction does not affect the calculated

TABLE II: Representative Data for Reaction 1 at 297 K in N₂

<i>P</i> (Torr)	(CH ₄) ₀ (ppm)	(Cl ₂) ₀ (ppm)	O ₂ /Cl ₂	ΔCH ₄ ^a (ppm)	CH ₃ Cl ^b (ppm)	time ^c (s)	<i>k</i> ₁ / <i>k</i> ₂ ^d
3.4	23700 ^e	32000	30.3	2500	900	40	0.036
3.4				4760	1336	85	0.034
6.2				2630	658	40	0.064
6.2				5050	1025	90	0.055
25				2490	390	50	0.124
25				4290	543	90	0.123
25	2672	6950	3.9	243	133	12	0.120
100				302	113	16	0.269
90	3509	3614	22.0	762	64	110	0.249
100	2437	6093	4.0	262	97	15	0.268
700				292	70	20	0.524
740 ^f	3100	6780	4.0	514	107	150	0.530
750 ^f	2632	6580	4.0	314	80	110	0.490
10530 ^{f,h}				278	57	150	0.705
10100 ^{f,h}				380	70	212	0.697
750 ^f	264	607	4.0	23	6.2	150	0.501
750 ^f				73	11.5	480	0.517
10650 ^{f,i}				39	6.9	160	0.726
10300 ^{f,i}				110	8.3	480	0.776
750 ^f	528	1214	15.4	83	6.1	200	0.530
10750 ^f				69	4.1	180	0.727
10200 ^f				133	5.3	360	0.770

^a Amount of CH₄ consumed during the irradiation. ^b Mole fraction of CH₃Cl formed. ^c Irradiation time. ^d Calculated rate constant ratio. ^e Each entry showing a new set of initial reactant concentrations represents a new mixture. Data sets with no initial concentrations specified are multiple determinations of *k*₁/*k*₂ using the mixture specification on a line above the entry. Unless specified otherwise, the reactor used is the jacketed-Pyrex vessel. For each mixture, N₂ was added to reach the specified pressure. ^f Experiment performed in the steel reactor. ^h Estimated UV absorbance across reactor = 80%. ⁱ Estimated UV absorbance across reactor = 20%.

rate constant ratio to within the data scatter. The value of *k*₁/*k*₂ in the mechanism was adjusted until the observed ΔCH₄ and [CH₃Cl] were obtained.

Table II presents data at 297 K for N₂ (or O₂) diluent at six pressures, which span the full pressure range studied. Because of the large number of data points, only these representative data are presented in tabular form; all other data are presented only as rate constant ratios in the figures. The data in Table II span a wide range of initial conditions: O₂/Cl₂ (4–30), Cl₂/CH₄ (1–2.6), ΔCH₄/(CH₄)₀ (0.1–0.4). No difference in the rate constant ratios is observed over these ranges of initial conditions, which supports the validity of the mechanism used to analyze the data. (See the discussion of mechanism validation and the additional data presented in the Appendix.) At 750 Torr, experiments were performed in both the Pyrex and steel reactors (see Table I); identical rate constant ratios were obtained in the two reactors. This indicates that heterogeneous reactions are negligible as was seen in the study of reaction 3. In all analyses, the efficiencies of N₂ and O₂ are assumed equal. The data at 25 Torr support this assumption because mixtures with predominantly O₂ or N₂ diluent gave indistinguishable rate constant ratios to within the data scatter. Finally, at 10⁴ Torr, one reaction mixture had a high initial Cl₂ density which resulted in a UV absorbance of 80% across the reactor. Model calculations indicated that this should not affect the calculated rate constant ratio to within experimental error. In fact, the rate constant ratios near 10⁴ Torr presented in Table II are independent of absorbance across the reactor, verifying this model calculation.

Figure 2 presents the values of *k*₁/*k*₂ determined at 297 K for N₂, He, and SF₆ diluents. The absolute value of *k*₁ can be determined from these data using the value of *k*₂ (=1.61 × 10⁻¹² cm³ molecule⁻¹ s⁻¹) verified in section A. To determine (*k*₁)₀ and (*k*₁)_∞, the data in N₂ and SF₆ diluents were fitted to the full Troe expression¹¹ using the center broadening factor (=0.46) determined for this reaction by Patrick and Golden.¹² The fitting program used was that contained in the "Sigmaplot" graph

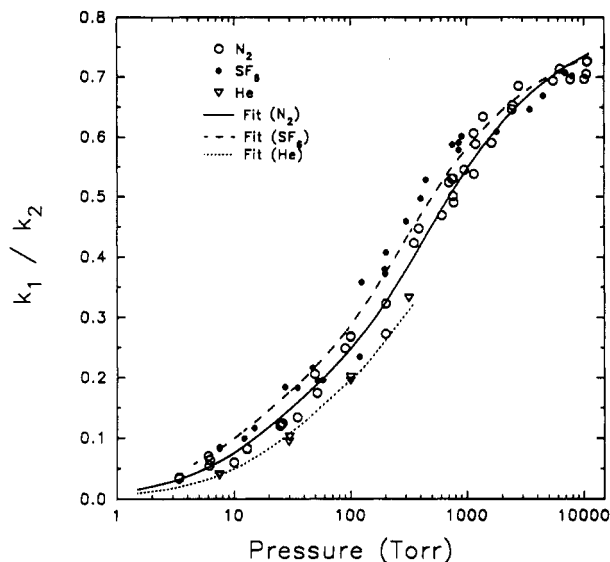


Figure 2. Relative rate constant ratios *k*₁/*k*₂ measured in He, N₂, and SF₆ diluents at 297 K. The lines represent Troe fits as discussed in the text.

TABLE III: High- and Low-Pressure Limiting Rate Constants for Reaction 1

<i>T</i> (K)	diluent	(<i>k</i> ₁) ₀ (cm ⁶ molecule ⁻² s ⁻¹)	(<i>k</i> ₁) _∞ (cm ³ molecule ⁻¹ s ⁻¹)
297	He	(4.22 ± 0.3) × 10 ⁻³¹ ^a	1.34 × 10 ⁻¹² ^b
297	SF ₆	(1.14 ± 0.2) × 10 ⁻³⁰	(1.30 ± 0.1) × 10 ⁻¹²
297	N ₂ (O ₂)	(7.48 ± 0.8) × 10 ⁻³¹	(1.34 ± 0.08) × 10 ⁻¹²
264	N ₂ (O ₂)	(1.23 ± 0.4) × 10 ⁻³⁰	(1.03 ± 0.2) × 10 ⁻¹²
370	N ₂ (O ₂)	(4.26 ± 1.7) × 10 ⁻³¹	(1.59 ± 0.5) × 10 ⁻¹²
297 (CD ₃) ^c	N ₂ (O ₂)	(11.8 ± 1.6) × 10 ⁻³¹	(1.38 ± 0.1) × 10 ⁻¹²

^a Error = 2 statistical standard deviations plus uncertainty in *k*₂ (5% at 297 K; 20% at 264 and 370 K). ^b For the He diluent, the high-pressure limit was fixed at the value for N₂. ^c This row presents the rate constants for CD₃; all other entries are for CH₃.

system.¹⁵ Because the pressure range of the He data is much more limited, the value of (*k*₁)_∞ in N₂ was used in the He data fit with (*k*₁)₀ as the only adjustable parameter. The values of the limiting rate constants are presented in Table III. The uncertainty in *k*₂ was combined with the statistical error in *k*₁/*k*₂ to obtain the overall error using the conventional propagation technique. These limiting rate constants were used in the Troe equation to generate the curves in Figure 2.

Cobos et al.² estimated a value of *F*_{cent} = 0.27 in fitting their data at 297 K. Using this relatively low value of *F*_{cent} would increase the calculated values of (*k*₁)_∞ and (*k*₁)₀ by factors of 1.09 and 2.6, respectively. Thus, the value of (*k*₁)_∞ is very insensitive to the choice of *F*_{cent}, but the low-pressure limiting rate constant is strongly correlated with it. The data in Figure 2 at 297 K in N₂ were also subjected to a three-parameter fit including *F*_{cent} as a variable. The value of *F*_{cent} deduced from this fit (0.48 ± 0.09) agrees with the theoretical estimate of Patrick and Golden. However, the quality of the fit is quite similar for both choices of *F*_{cent}, and the data are deemed insufficient, particularly at the low-pressure end, to test the value of *F*_{cent} accurately.

The values of (*k*₁)_∞ determined in N₂ and in SF₆ diluents are identical to within experimental error, as expected if the high-pressure limit is being determined correctly. The low-pressure limiting rate constants, however, show evidence of different deactivation efficiencies, assuming that the value of *F*_{cent} is independent of diluent. Based on the low-pressure-limiting rate constants in Table III, the relative efficiencies (He:N₂:SF₆) are (0.56:1.0:1.52).

The measured rate constant ratios at 264 and 370 K are presented in Figure 3. Values of *k*₁ were calculated from these

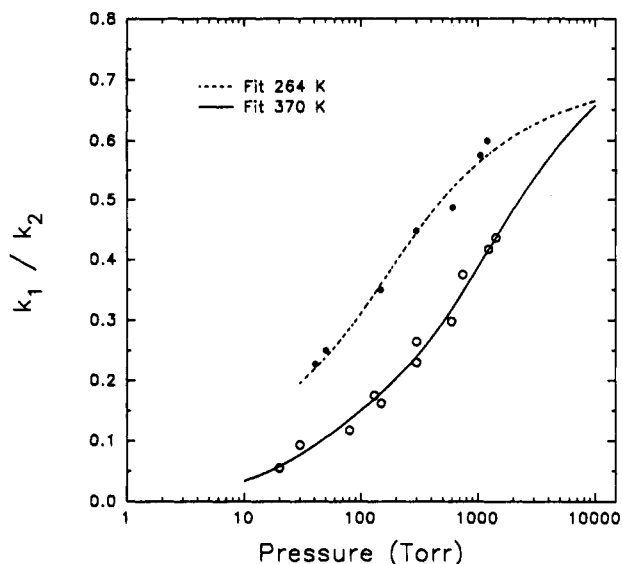


Figure 3. Relative rate constant ratios k_1/k_2 measured in N₂ at 264 and 370 K. The lines represent Troe fits using constants discussed in the text.

two sets of data using the temperature-dependent expression for k_2 discussed above [$=3.94 \times 10^{-12} \exp(-530/RT)$]. These rate constant vs pressure curves were then fitted to a Troe expression as in the case of the 297 K data except that center broadening factors of 0.48 and 0.42 were used at 264 and 370 K, respectively. These values were estimated by a linear extrapolation of the values of F_{cent} at 200 and 300 K calculated by Patrick and Golden.¹² The limiting rate constants determined by this method are presented in Table III with the uncertainty estimated as discussed above. The Troe curves generated by these limiting rate constants are included in Figure 3.

These temperature-dependent limiting rate constants were fitted to the non-Arrhenius expression used by Keiffer et al.¹ by weighting the significance of each rate constant by the inverse of the stated uncertainty. The results of these fits (errors include 5% in k_2):

$$(k_1)_0 = (7.56 \pm 1.1) \times 10^{-31} (T/300)^{-3.64 \pm 1.0} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$$

$$(k_1)_\infty = (1.31 \pm 0.1) \times 10^{-12} (T/300)^{1.2 \pm 0.8} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The temperature exponents agree with those derived over the range 334–582 K in Ar by Keiffer et al.¹ (-3.3 ± 0.4 and 1.2 ± 0.4 , respectively).

Figure 4 presents a comparison of the current relative rate determinations of k_1 as a function of pressure in Ar and He diluents to the absolute measurements by other research groups. The data obtained in argon agree exactly with the measurements (32–488 Torr) of Pilling and Smith¹⁶ after reducing all values in their Table I by the 5% correction derived from their later "global" fitting technique.¹⁷ This agreement coupled with the above measurements of the rate of reaction 3 show that the data of Pilling and Smith¹⁶ and Davies et al.⁵ for reactions 1 and 3, respectively, are exactly consistent with one another as tested by these relative rate measurements. The current Ar data are approximately 25% lower than the data (167–800 Torr) of Cobos et al.² In He diluent, the data at 8 Torr and the Troe fit to the current data agree very well with the measurements of Plumb and Ryan (1–7 Torr).¹⁸ For use in Figure 4, the total pressures for the data of Plumb and Ryan in their Figure 6a (which contains a small amount of O₂) have been corrected to a pure He total pressure using the ratio of efficiencies (He/N₂ = 0.56) quoted above. This produces a correction of approximately 18% in the

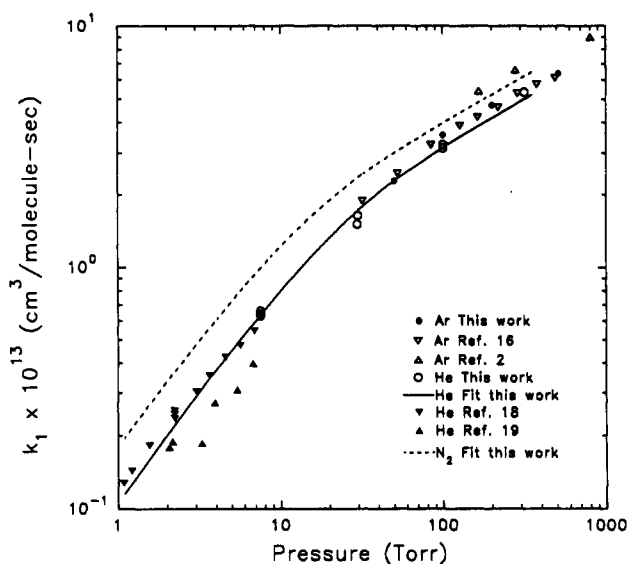


Figure 4. Comparison of rate constants determined from k_1/k_2 at 297 K in He and Ar diluents with absolute measurements from other references. Also included are lines representing the Troe fits to the He and N₂ data in Figure 2. In He diluent, four measurements were made at 7.5 Torr with a scatter of $\pm 2\%$.

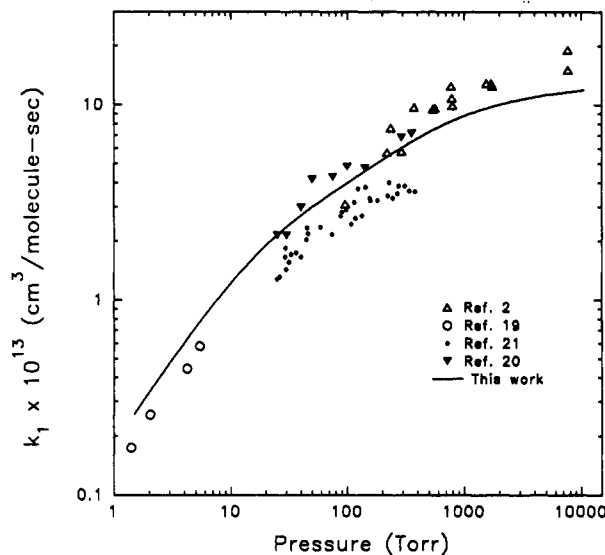
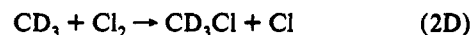


Figure 5. Comparison of rate constants determined from k_1/k_2 at 297 K in N₂ diluent with absolute measurements from other references. The solid line represents the Troe fit to the N₂ data in Figure 2.

total pressure at 1 Torr and 2% at 7 Torr. Thus, the correction is small over their pressure range. The current data are approximately 30% higher than the data of Selzer and Bayes,¹⁹ which show approximately $\pm 30\%$ scatter.

A comparison of the relative rate determination of k_1 to absolute measurements of this rate constant in N₂ at 297 K is shown in Figure 5. The solid line is derived from the Troe fit using the rate constants in Table III. The current relative rate data are consistent with the absolute rate measurements,^{19–21} which scatter around the line generally to within $\pm 30\%$. The data of Cobos et al.,² which agree reasonably with the relative rate measurements at 100–200 Torr, are approximately 50% higher at 10⁴ Torr.

C. CD₃ + O₂ Reaction. In addition to the above experiments, the relative rate constant ratio k_{1D}/k_{2D} was measured in N₂ diluent only:



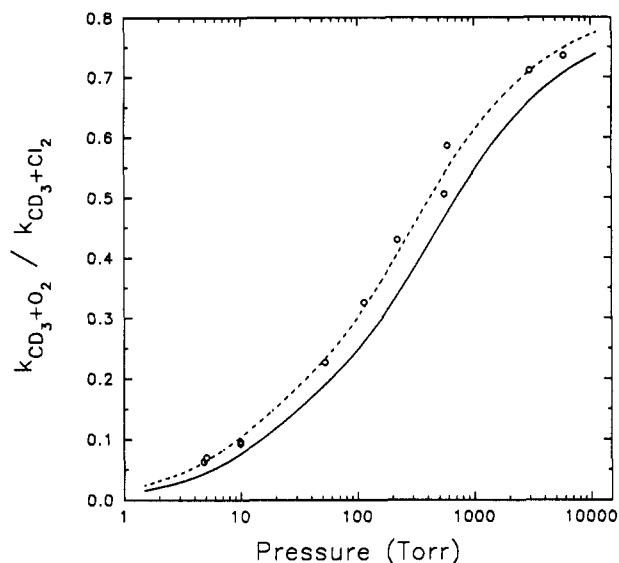


Figure 6. Relative rate constant ratios k_{1D}/k_{2D} in N_2 diluent at 297 K. The dashed line is derived from the Troe fit to the data using the parameters presented in the text. The solid line is the Troe fit to the k_1/k_2 data in Figure 2.

In these experiments, mixtures of CD_4 , Cl_2 , O_2 , and N_2 were irradiated and then analyzed for ΔCD_4 and $[CD_3Cl]$. The rate constant ratio was then calculated by a computer simulation similar to that for CH_4 . The major change required in this model was substitution of k_{5D} ($=6.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)²² and k_{6D}/k_{5D} ($=13.6 \pm 0.5$). The latter ratio was measured in the Pyrex reactor during these experiments by irradiating two mixtures at reactor pressures between 40 and 500 Torr: (1) 1382 ppm CD_4 , 13 355 ppm CD_3Cl , 26 315 ppm Cl_2 , balance N_2 ; (2) 1419 ppm CD_4 , 1324 ppm CD_3Cl , 2790 ppm Cl_2 , balance O_2 . Two irradiation experiments were performed with mix 2 and four with mix 1. In these experiments, approximately 10% of the CD_4 and 70–80% of the CD_3Cl were consumed. Computer fits were used in evaluating the results from mixture 2 to properly account for formation of CD_3Cl from CD_4 . The measured ratios, k_{6D}/k_{5D} , were independent of the mixture composition and the total pressure in these experiments. This result has been quoted as a private communication in ref 22 and is consistent with the measurements by FTIR spectroscopy in that reference.

Values of k_{1D}/k_{2D} were obtained by irradiating three mixtures with the respective composition ratios: O_2/Cl_2 ($=12.3, 60.8, 1380$); CD_4/Cl_2 ($=1.0, 1.0, 1.0$); O_2 ($=2\%, 96.6\%, 99.9\%$); N_2 ($=98\%, 0\%, 0\%$). Consumption of the initial CD_4 ranged from 10 to 30%. The calculated rate constant ratio was independent of mixture composition and CD_4 consumption. The rate constant ratios determined in these experiments are presented in Figure 6.

The rate constant k_{2D} , which is required to calculate absolute values of k_{1D} , has not been measured. However, this is an abstraction reaction, and no large isotope effect is expected. Several other rate constants for abstraction reactions by CH_3 and CD_3 have been measured which support this contention. Timonen et al.²³ measured the rate constants for reaction of CH_3 and CD_3 with Br_2 and found that there was an insignificant isotope effect ($CD_3/CH_3 = 1.16 \pm 0.16$). Nicovich et al.²⁴ found similar results in their determination of the rate of hydrogen abstraction from HBr by these radicals at 297 K ($CD_3/CH_3 = 1.13 \pm 0.15$). Finally, the data at 300 K obtained by Seetula et al.²⁵ and Donaldson and Leone²⁶ for the abstraction of H from HI by CH_3 and CD_3 , respectively, again show no significant isotope effect ($CD_3/CH_3 = 0.95 \pm 0.3$).

Based on these analogous reactions, the value $k_{2D} = k_2$ has been assumed in determining absolute values of k_{1D} . The data in Figure 6 have been fitted to the Troe expression with $F_{cent} =$

0.46, yielding the values of $(k_{1D})_0$ and $(k_{1D})_\infty$ presented in Table III. Based on the above assumption for k_{2D} , the value of $(k_{1D})_\infty$ is identical to that for CH_3 . The low-pressure limiting rate constant for CD_3 is approximately 50% larger than that of CH_3 , which may reflect a more efficient energy partitioning by the low-frequency vibrational modes in the CD_3O_2 radical.

Summary and Conclusions

A relative rate technique has been used to determine the pressure dependence of the rate constant of the addition reaction of O_2 to CH_3 (k_1). In these experiments, k_1 was measured relative to that of the reaction of CH_3 with Cl_2 (k_2). Because an accurate value of k_2 is required in order to determine the value k_1 from the relative rate data, the value of k_2 used in the evaluation was also tested against available data at pressures up to 600 Torr. By measuring the ratio k_3/k_2 , the value of k_2 was found to be consistent with recent precise measurements of the rate of addition of NO to CH_3 (k_3). This cross comparison provides strong evidence that accurate values of k_1 can be obtained from the relative rate measurements using this reference reaction.

Values of k_1 were obtained from these measurements over the pressure range 3–11 000 Torr in N_2 diluent at 297 K. These data represent the most extensive determination of the pressure dependence of k_1 in a single, self-consistent series of experiments, leading to a Troe expression which agrees with the data to within $\pm 10\%$ over the full pressure range. As such, they provide the best available high-pressure limiting rate constant for reaction 1. The value of $(k_1)_\infty$ ($=1.34 \pm 0.1$) $\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is well determined in these experiments and is not dependent to within experimental error on the choice of F_{cent} over a range of a factor of 1.7. This value of $(k_1)_\infty$ agrees with the determination of Keiffer et al.¹ ($=1.2 \pm 0.2$) $\times 10^{-12}$) but is smaller than that obtained by Cobos et al.² ($=2.2 \pm 0.3$) $\times 10^{-12}$). Because Cobos et al. observe no increase in k_1 at pressures above 10 atm, this difference cannot be ascribed to the fact that the current relative rate measurements are limited to 10 atm. In addition, less than 10% of the discrepancy results from the different choice of center broadening factor (see section B). Measurements in SF_6 diluent give the same high-pressure-limiting rate constant, lending support to the value determined in these experiments.

The value of $(k_1)_0$ is correlated with the value of F_{cent} and could be in error if the theoretical calculation of F_{cent} is incorrect. Measurements in He, N_2 , and SF_6 diluents result in calculated third-body efficiencies for these species of 0.56:1.0:1.52, assuming that F_{cent} is the same for all diluents. These efficiencies are similar to those (0.47:1.0:1.2) estimated for reaction 3 in a recent compilation.²⁷ The results in N_2 as well as in He and Ar generally agree to within $\pm 35\%$ with the absolute measurements of this rate constant at 297 K by other research groups over much more limited pressure ranges. These earlier data scatter randomly around the current measurements. The most precise absolute measurements are in near perfect agreement with the current data.

Experiments at 264, 297, and 370 K were used to derive the temperature dependencies of $(k_1)_\infty$ and $(k_1)_0$. The exponents of the non-Arrhenius factor ($T/300$) in each of these expressions (1.2 ± 0.8 and -3.6 ± 1.0 , respectively) are identical to those measured by Keiffer et al.¹ in Ar (1.2 ± 0.4 and -3.3 ± 0.4) to within experimental error. They are also very similar to the values (0.6 and -3.5) derived for reaction 3 by Jodkowski et al.²⁷

Appendix I. Validation of Kinetic Mechanism

During the review of this manuscript, concern was expressed about the validity of the statement that CH_3 is consumed solely by O_2 and Cl_2 in these experiments. This fact is of central importance to the interpretation of relative rate data and will be examined in more detail within this Appendix.

To my knowledge, the best proof that CH₃ is consumed only by reaction with Cl₂ and O₂ in this relative rate study lies in the observation that the rate constant ratios are independent of mixture composition as well as other experimental conditions such as light intensity and percentage consumption of methane. As an example, reducing the methane concentration while keeping that of Cl₂ and O₂ constant would reduce the consumption of CH₃ radicals by stable products if such reactions are important and would change the apparent calculated rate constant ratio. Similarly, reducing the light intensity reduces the steady-state concentration of free radicals, and if free-radical reactions were important paths of CH₃ removal, the apparent rate constant ratio would vary with light intensity. Finally, the rate constant ratio should be independent of the relative concentration of Cl₂ and O₂. If another sink for CH₃ were important, the calculated value of k_1/k_2 would change with Cl₂/O₂.

In the main body of the text, I stated that mixture composition had been varied over substantial ranges, but this fact was not discussed in detail. In addition, the concentration ranges, particularly Cl₂(and O₂)/CH₄, were not as broad as was possible, and the UV light intensity was not varied within one reactor, although the intensity did differ by a factor of 7 between the two reactors. For inclusion in this Appendix, new data have been generated which expand these important verifications of the mechanism. Data have been obtained both in a third Pyrex reactor and in the same stainless steel reactor approximately 30 months after the experiments in the main body of the paper.

Experiments were carried out near 1-atm total pressure in a cylindrical (2-cm i.d.) Pyrex reactor with a total volume of 100 cm³ and a temperature of 297 K. In these experiments, the Cl₂/CH₄ ratio was increased to 12.6, a factor of 5 increase above the ratio used in the measurements at this pressure in Table II. In addition, two UV intensities were tested which differed by approximately a factor of 100, as determined by the factor of 100 longer irradiation time necessary to reach the same CH₄ consumption. The data in Table IV show that the average rate constant ratio for four runs near 700 Torr is 0.48, in excellent agreement with the value of 0.495 in Figure 2. Note that the ratio is independent of UV intensity and, in combination with data in Table II, Cl₂/CH₄ ratio. The data in Table II had already shown that k_1/k_2 is independent of O₂/Cl₂ over a factor of 4 at this pressure.

At 6000 Torr, supplemental experiments were performed in which O₂/Cl₂, Cl₂/CH₄, and UV intensity were varied over substantial ranges in the steel reactor. The average of the seven experiments presented in Table IV gives $k_1/k_2 = 0.7 \pm 0.03$, which agrees with the value of 0.71 at this pressure in Figure 2. Including the earlier results at this pressure using mixtures similar to those for 10⁴ Torr in Table II, the measured rate constant ratios are independent of O₂/Cl₂ (=4–39) and Cl₂/CH₄ (=2.3–36). The rate constant ratio is also independent of UV intensity, which was decreased by factors of approximately 10 and 100 during these experiments relative to the standard intensity with no filter present. Again no variation in rate constant ratio is observed to within the 5% uncertainty for single measurements. Finally, k_1/k_2 is independent of the percentage consumption of CH₄ over the range 3.6–62%. (Note that at 3.6 ± 0.5% conversion the error [±15% of the CH₄ consumed] is somewhat greater than for larger consumption because of the difficulty of measuring very small degrees of consumption.)

The expected stable primary products from this oxidation reaction are CH₃OH, CH₂O, CH₃OOH, formed from peroxy radical reactions, CH₃Cl, and HCl. Of these products, only HCl reacts at an appreciable rate with methyl radicals ($k = 4.7 \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹), and at typical concentrations in Table II this will contribute less than 0.1% to the total CH₃ consumption. The other stable products react much more slowly. CH₃ does react rapidly with peroxy radicals, particularly CH₃O₂ (9×10^{-11}).

TABLE IV: Representative Data for Reaction 1 at 297 K in N₂

P (Torr)	(CH ₄) ₀ (ppm)	(Cl ₂) ₀ (ppm)	O ₂ /Cl ₂	ΔCH ₄ ^a (ppm)	CH ₃ Cl ^b (ppm)	time ^c (s)	k_1/k_2 ^d
700	555 ^e	7020	3.76	102.1	23.2	30	0.47
600				104.3	23.4	3060 ^f	0.47
755	278	3519	3.76	40.0	9.9	22	0.48
				46.1	10.6	2220 ^f	0.49
6000	100.4	1029	38.6	61.9	0.32	300	0.75
				8.6	0.253	100	0.73
				3.6	0.148	60	0.64
6000	49.1	1784	11.1	15.4	0.76	120	0.71
				4.0	0.37	75	0.72
				8.0	0.62	1200 ^g	0.68
				3.0	0.31	12000 ^h	0.67

^a Amount of CH₄ consumed during the irradiation. ^b Mole fraction of CH₃Cl formed. ^c Irradiation time. ^d Calculated rate constant ratio. ^e Each entry showing a new set of initial reactant concentrations represents a new mixture. Data sets with no initial concentrations specified are multiple determinations of k_1/k_2 using the mixture specification on a line above the entry. The reactor used is a Pyrex vessel for 1-atm data; for the high-pressure data the steel reactor was used. For each mixture, N₂ was added to reach the specified pressure. ^f UV intensity reduced by a factor of approximately 100 by placing a 0.75-in.-thick plexiglass sheet between reactor and lamp. ^g UV intensity reduced ×10 using a neutral density filter (ND 1). ^h UV intensity reduced ×100 using a neutral density filter (ND 2).

However, a full model calculation (using a mechanism including peroxy radical reactions, formation of HO₂, and consumption of products) for the second group of data at 6000 Torr in Table IV indicates that the steady-state concentrations of CH₃O₂ and HO₂ are 1.9×10^{12} and 0.7×10^{12} molecules cm⁻³, respectively. In these calculations, the Cl atom concentration was estimated from the rate of CH₄ decay. At these radical concentrations, CH₃ will react with Cl₂ approximately 4000 times faster than with CH₃O₂. Thus, no interference from radical–radical reactions in the calculation of k_1/k_2 would be expected to occur. Based on the model calculation, reduction of the light intensity by a factor of 100 reduces the CH₃O₂ radical concentration by a factor of approximately 6, allowing an experimental test of the presence of perturbations in the measured ratio by radical–radical reactions by varying the light intensity.

The fact that the rate constant ratio is independent of initial reactant ratios over factors of 10, UV intensity over a factor of 100, and percentage of CH₄ consumption over a factor of 20 provides strong experimental evidence that the CH₃ radicals produced react solely with O₂ and Cl₂. This verifies the estimates made from the full mechanism including the formation of methylperoxy radical reaction products discussed above. These products were not included in the simple fitting mechanism for determining k_1/k_2 because the estimates indicated that CH₃ would not react with any of these products or free radicals at a rate sufficient to perturb the calculation of k_1/k_2 .

The fact that the calculated value of k_1/k_2 is independent of percentage of methane consumption over a factor of 20 also verifies that the ratio k_6/k_5 used in the model is correct to within the experimental error in the k_1/k_2 determination and that consumption of Cl₂ and O₂ does not perturb the calculation to within experimental error. Knowledge of the ratio k_6/k_5 is critical because CH₃Cl reacts 5 times faster with Cl than does CH₄, and substantial CH₃Cl consumption occurs during these studies. If the ratio k_6/k_5 were not correct in the fitting mechanism, the calculated value of k_1/k_2 would vary with percentage of CH₄ consumption. As an example, an error of 8% in the value of k_6/k_5 (that quoted in ref 13) would result in a 3% error in k_1/k_2 after 10% CH₄ consumption and a 14% error after 50% consumption. Thus, the apparent rate constant ratio would vary by 10% over this range of consumption. No systematic variation of this magnitude is observed, and in fact, most measurements have been made near 10% CH₄ consumption where an 8% uncertainty in k_5/k_6 would produce only a 3% error in k_1/k_2 .

If no consumption of CH₃Cl occurred, the relative rate constant ratio could be calculated from the simple expression

$$\frac{k_1}{k_2} = \frac{[\Delta\text{CH}_4] - [\text{CH}_3\text{Cl}]}{[\text{CH}_3\text{Cl}]} \frac{[\text{Cl}_2]}{[\text{O}_2]}$$

This is derived from reactions 1 and 2, which are the only sinks for methyl radicals. However, substantial CH₃Cl loss can occur via reaction 6 in these experiments, particularly for larger percentages of CH₄ consumption, and for this reason, a computer fit was used instead of the analytic expression to calculate k_1/k_2 accurately.

In summary, the wide range of experimental conditions included in these experiments provides strong verification of the rate constant ratios presented in this publication. I believe that these results leave little doubt that the CH₃ radical is consumed solely by reaction with Cl₂ and O₂ to within the measurement error. Also, the fact that the ratios determined remain identical over 2 years and in three different reactors with different surfaces provides substantial evidence that the reactions are homogeneous and very reproducible.

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