## RATE CONSTANT FOR THE REACTION OF N(4S) WITH CH<sub>3</sub> AT 298 K

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The absolute rate constant for the reaction of N(<sup>4</sup>S) with CH<sub>3</sub> has been determined at 298 K in a discharge flow system coupled with collision-free sampling mass spectrometry at low electron energies. The rate constant was determined under pseudo-first-order conditions with [N] > [CH<sub>3</sub>]. The result is  $k_1 = (8.6 \pm 2.0) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. This is compared to a previous estimated value as well as values of rate constants for other atom+radical reactions.

#### 1. Introduction

Reactions of methyl radicals with oxygen and nitrogen atoms are important in a variety of phenomena. The reaction  $O+CH_3 \rightarrow H_2CO+H$  is important in both hydrocarbon combustion kinetics [1] and the photochemistry of the upper atmosphere of the Earth [2]. The kinetics of this reaction have been extensively investigated [1,3,4] from 200 to 2300 K. In marked contrast, there is little information concerning the reaction of ground state N(<sup>4</sup>S) with CH<sub>3</sub>. It has been suggested that the process is important in the reaction of active nitrogen with hydrocarbons [5,6] and in models for the atmosphere of Titan [7,8]. Possible reaction channels include

 $N + CH_3 \rightarrow HCN + 2H, \qquad (1a)$ 

 $N+CH_3 \rightarrow HCN+H_2 , \qquad (1b)$ 

 $N + CH_3 \rightarrow H_2 CN + H.$  (1c)

Formation of HCN in this reaction is an important aspect of both the active nitrogen/hydrocarbon system and the Titan atmospheric model. A very rough estimate of  $k_1$  by Armstrong and Winkler [5] employed an Arrhenius A factor of  $5 \times 10^{-11}$  to  $5 \times 10^{-13}$  and a small activation energy of  $0.5 \pm 0.4$  kcal/mole.

In their model of the atmosphere of Titan, Yung et al. [8] chose the upper limit to A, and E=0.5 kcal/ mole; this yields a value for  $k_1$  at 300 K of  $2.2 \times 10^{-11}$ cm<sup>3</sup> s<sup>-1</sup>. Because of the importance of this reaction in models of the atmosphere of Titan and the lack of quantitative kinetic data, we have initiated a study of the kinetics of the N+CH<sub>3</sub> reaction. We report here a direct measurement under pseudo-first-order conditions of  $k_1$  at 298 K.

# 2. Experimental

All of the experiments were performed using the discharge flow-mass spectrometry apparatus described in detail previously [9]. Briefly, the flow tube consisted of 3 cm diameter, uncoated Pyrex glass and was approximately 60 cm in length. Time resolution was achieved by means of a movable injector, and relative concentrations of reactants and products were measured by a quadrupole mass spectrometer (Extranuclear Laboratories, Inc.) operating at low electron energies. Experiments were typically performed at 1 Torr total pressure and a linear flow velocity of  $\approx 2200$  cm s<sup>-1</sup>. Some experiments were carried out at pressures between 0.3 and 1.6 Torr. Flows of He, N<sub>2</sub> and other reagents (CF<sub>4</sub>, CH<sub>4</sub>, CD<sub>2</sub>H<sub>2</sub>, CD<sub>3</sub>H, NO and Cl<sub>2</sub>, each diluted in He) were measured and controlled by separate flow controllers (ASM International N.V.).

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Atomic nitrogen was generated by passing  $N_2$  (1-10%, diluted in He) through a microwave discharge (70 W, 2450 MHz). After the discharge, excited N and N<sub>2</sub> were quenched in a recombination volume [9-11] (10 cm long, 7 cm diameter Pyrex glass) which had a residence time of  $\approx 60$  ms. In some of the experiments the flow of helium through the discharge was reduced, and the residence time was increased to as much as  $\approx 1$  s. N-atom concentrations were determined using the N+NO titration reaction. Sufficient NO was added through the movable injector to destroy all of the N atoms, which could be monitored by their signal at m/e=14 (electron energy = 16 eV). The change in NO concentration on turning off the discharge was calculated from the difference in the signal at m/e=30 (electron energy = 13.5 eV) and the known NO flow. This change is equal to the N-atom concentration.

Methyl radicals were monitored at m/e=15 using low electron energies ( $\approx 13$  eV) to minimize fragmentation of CH<sub>4</sub>. The radicals were generated chemically in about 1 ms by the reaction

$$F+CH_4 \rightarrow HF+CH_3$$
, (2)

which has a rate constant [2]  $k_2(298 \text{ K}) =$  $8.0 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>. Excess CH<sub>4</sub> ([CH<sub>4</sub>]/[F]  $\approx 100$ ) was added through the movable injector to a stream of F atoms. The atomic species were generated by passing  $CF_4$  ( $\approx 0.1\%$  diluted in He) through a microwave discharge (70 W, 2450 MHz) [3]. The discharge tube was uncoated alumina, coupled to the glass system with Teflon quick-connects. Downstream of the discharge, a recombination volume allowed sufficient time to destroy species such as  $CF_2$  and  $CF_3$  which are formed in the discharge. Because F atoms are converted stoichiometrically to  $CH_3$ ,  $[CH_3]$  can be obtained directly from a knowledge of [F]. F-atom concentrations were determined using the  $F+CH_4$  reaction in a method directly analogous to that used for the measurement of N atoms, which was described in section 1. CH<sub>4</sub> was monitored at m/e=16 (electron energy =16 eV). Measured methyl concentrations were in the range  $3 \times 10^{11}$  to  $1 \times 10^{12}$  cm<sup>-3</sup>, and the minimum detectable concentration was  $\approx 10^{10}$  cm<sup>-3</sup> at a signal-to-noise ratio of 1, and 10 s integration time.

Helium (99.999%, Air Products) was dried by passage through a molecular sieve trap at 77 K be-

fore entering the flow system. NO (99%, Matheson C.P.) was purified by successive distillations at 143 K and collected at 77 K.  $Cl_2$  (99.9%, Matheson UHP) used for the  $CH_3 + Cl_2$  rate measurement and  $CF_4$  (99.9%, Matheson) were degassed at 77 K.  $N_2$  (99.999%, Scientific Gas Products UHP),  $CH_4$  (99.97%, Matheson UHP),  $CD_2H_2$  and  $CD_3H$  (98%, MSD Isotopes) and  $Cl_2$  (3.5% in helium, Matheson) for pretreatment of the flow tube walls were each used without purification.

## 3. Results

The reaction of N(<sup>4</sup>S) with CH<sub>3</sub> was studied under pseudo-first-order conditions at 298 K with  $[N] > [CH_3]$ . The course of the reaction was followed by monitoring the decay of CH<sub>3</sub> with reaction time. The determination of the bimolecular rate constant depends on quantitative measurement of the exponential decay of CH<sub>3</sub>, the absolute concentration of N and the reaction time. In order to assess the reliability of the CH<sub>3</sub> decay rates, we made a few measurements at 298 K of the rate constant for the reaction

$$CH_3 + Cl_2 \rightarrow CH_3Cl + Cl, \qquad (3)$$

while rate constant measurements for

$$\mathbf{N} + \mathbf{NO} \rightarrow \mathbf{N}_2 + \mathbf{O} \tag{4}$$

helped us to assess the quantitative reliability of our production and measurement of [N]. For reaction (3), we performed six experiments with  $[CH_3] =$  $1.5 \times 10^{12}$  cm<sup>-3</sup> and [Cl<sub>2</sub>] between  $4.9 \times 10^{13}$  and  $2.1 \times 10^{14} \text{ cm}^{-3}$ . The result is  $k_3 = (1.2 \pm 0.2) \times 10^{-12}$ cm<sup>3</sup> s<sup>-1</sup> (2 $\sigma$ ). This is in good agreement with the value  $(1.5\pm0.1)\times10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> reported by Kovalenko and Leone [12] and in moderate agreement with the somewhat higher value of  $(2.0\pm0.4)$  $\times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> of Timonen and Gutman [13]. In the case of reaction (4), there were a total of eight measurements with [NO] =  $3.2 \times 10^{11}$  or  $1.0 \times 10^{12}$ cm<sup>-3</sup> and [N] ranging from  $2.3 \times 10^{12}$  to  $1.8 \times 10^{13}$ cm<sup>-3</sup>. Our result is  $k_4 = (3.2 \pm 0.6) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup>  $(2\sigma)$  in excellent agreement with the value  $k_4 = (3.4 \pm 1.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  from the 1985 NASA panel recommendation [2]. Neither of these studies is sufficiently detailed to constitute new determinations of k(298 K) for  $CH_3 + Cl_2$  or N + NO. However, the agreement with published values demonstrates the quantitative reliability of our measurements of  $CH_3$  decay and [N] required for the present study of the  $N + CH_3$  reaction.

The exponential first-order decay constants,  $k_{obs}$ , were obtained as the slopes of plots of  $\ln(CH_3 \text{ sig$  $nal})$  versus reaction time. Typical decays are displayed in fig. 1. These plots show good linearity, indicating the absence of interference from secondary chemistry. Values for  $k_{obs}$  were corrected (2-20%) for axial diffusion as described elsewhere [9,14] to give  $k_{corr}$ .

A small stoichiometric correction (on the average  $\approx 5\%$ ) was made to  $[N]_0$  to yield  $[N]_{mean}$  according to the equation  $[N]_{mean} = [N]_0 - \frac{1}{2} [CH_3]_0$ . As previously described [9], this allows for depletion of N due to reaction with CH<sub>3</sub>. The occurrence of secondary reactions of the products of reaction (1) with N atoms would lead to a larger correction being required. Measurement of the change in signal at m/e=14 during experimental decays showed that these corrections would lead to a small increase in the overall measured rate constant, but such a correction has not been made in the absence of a better understanding of the products of reaction (1) and their secondary reactions. Table 1 summarizes the results of a total of 26 experiments which encompass



Fig. 1. Typical first-order logarithmic decay plots of CH<sub>3</sub> signal versus time in the presence of various concentrations of nitrogen atoms  $(10^{12} \text{ cm}^{-3})$ : (A) 0.97; (B) 1.82; (C) 6.26; (D) 9.80.

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variation of a large number of reaction parameters and conditions. Included are: variation of [N]/[CH<sub>3</sub>] from 2 to 22; variation of [N]<sub>mean</sub> by a factor of 15; variation of  $[CH_3]_0$  by a factor of 4; variation in total pressure from 0.3 to 1.6 Torr He; change in residence time in the N-atom expansion volume-bypass system from a typical value of 60 ms to  $\approx 1$  s; replacement of CH<sub>3</sub> by the isotopic variations CH<sub>2</sub>D (generated by F+CH<sub>2</sub>D<sub>2</sub>) and CD<sub>2</sub>H (generated by  $F+CH_2D_2$  and  $F+CD_3H$ ). None of these variations had any effect on the reaction kinetics. This is clearly shown in fig. 2, where a plot of  $k_{\text{corr}}$  versus [N]<sub>mean</sub> exhibits good linearity for all 26 experiments. The bimolecular rate constant was determined from the slope of the line in fig. 2 using linear least-squares analysis. The result is  $k_1 =$  $(8.56 \pm 0.86) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> (2 $\sigma$ ). Allowing for possible systematic errors gives the recommended value  $k_1 = (8.6 \pm 2.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . The intercept in fig. 2 is  $67 \pm 31$  s<sup>-1</sup>, in agreement with measurements of CH<sub>3</sub> decay made in the absence of N.

### 4. Discussion

Potential complications in this system include contribution from atomic or molecular excited states of nitrogen formed in the N<sub>2</sub> discharge or in the flow tube, presence of  $CF_3$  or  $CF_2$  in addition to F in the  $CF_4$  discharge, presence of NH and its contribution to the CH<sub>3</sub> signal at m/e=15 and occurrence of reactions of CH<sub>3</sub> other than with N(<sup>4</sup>S) and loss at the wall. Increasing the residence time in the N2 recombination volume from  $\approx 60$  ms to 1 s did not affect the results, indicating that metastable N<sub>2</sub> and N produced in the discharge are not contributing to the decay of CH<sub>3</sub>. Electronically excited N<sub>2</sub> generated by recombination in the flow tube can only be present in small concentration, as we obtained no signal at mass 28 when the N2 discharge was on, and the electron energy was below the threshold for ground state N<sub>2</sub>. Furthermore, homogeneous N-atom recombination is slow under our conditions and we were unable to measure a significant wall loss for N, suggesting that the generation of N<sub>2</sub><sup>\*</sup> by heterogeneous recombination is unimportant. The presence in the flow tube of CF<sub>3</sub> or CF<sub>2</sub> generated in the CF<sub>4</sub> discharge could slightly reduce [N]<sub>mean</sub> due to loss

$[N]_0 (10^{12} \text{ cm}^{-3})$	$[N]_{mean}$ (10 <sup>12</sup> cm <sup>-3</sup> )	$[CH_3]_0 (10^{11} \text{ cm}^{-3})$	P <sub>total</sub> (Torr)	$k_{\rm corr}^{a}$ (s <sup>-1</sup> )
3.63	3.40	4.59	1.04	340± 8
4.77	4.54	4.59	1.05	$380 \pm 10$
6.70	6.47	4.59	1.05	633±24
8.62	8.39	4.59	1.05	$709 \pm 16$
10.5	10.3	4.59	1.05	988±90
7.57	7.02	11.0	1.06	595±24
12.1	11.5	11.0	1.07	943±50
12.4	11.8	11.0	1.07	1105±65
14.8	14.2	11.0	1.07	1232±45
1.19	0.97	4.39	1.03	140± 4
2.04	1.82	4.39	1.04	$283 \pm 6^{b}$
6,48	6.26	4.39	1.04	712±29
10.0	9.80	4.39	1.08	972±64 <sup>b</sup>
1.06	0.94	2.46	0.52	174± 8
2.69	2.38	6.14	0.31	256± 6
5.98	5.67	6.14	0.73	$622 \pm 18$
6.76	6.45	6.14	0.32	556±27
8.67	8.36	6.14	0.74	814±18
3.06	2.62	8.72	1.58	217±14
5.56	5.12	8.72	1.61	423±16
5.83	5.58	5.0 °)	1.05	447±24 <sup>d</sup> )
5.83	5.58	5.0 °)	1.05	487±45°)
9.43	9.18	5.0 °)	1.05	951±41 <sup>d</sup> )
6.18	5.93	5.0 °)	1.06	$655 \pm 40^{\text{f}}$
6.23	5.98	5.0 °)	1.06	669±43 <sup>f</sup> )
6.99	6.74	5.0 °)	1.08	$755 \pm 28^{\text{f}}$

 Table 1

 Rate data for the reaction of N atoms with methyl radicals

<sup>a)</sup> Uncertainty in  $k_{corr}$  is twice the standard deviation.

<sup>b)</sup> Residence time in the  $N_2$  discharge recombination volume increased from 60 ms to  $\approx 1$  s.

c) Total methyl radical concentration estimated from flow of CF4 and comparison with similar experiments.

<sup>d)</sup> CH<sub>2</sub>D formed by  $F+CH_2D_2 \rightarrow CH_2D+DF$  and monitored at m/e=16.

<sup>e)</sup> CD<sub>2</sub>H formed by  $F+CH_2D_2 \rightarrow CD_2H+HF$  and monitored at m/e=17.

<sup>f)</sup> CD<sub>2</sub>H formed by  $F+CD_3H\rightarrow CD_2H+DF$  and monitored at m/e=17.

of N(<sup>4</sup>S), in addition to the already allowed-for loss due to reaction with CH<sub>3</sub>. However, Plumb and Ryan [3] have shown that increased residence time in the CF<sub>4</sub> discharge reduces [CF<sub>3</sub>] and [CF<sub>2</sub>] to the point where they are not detectable, while reducing [F] by only a factor of 2. We were not able to detect CF<sub>3</sub> or CF<sub>2</sub> as products of our CF<sub>4</sub> discharge expansion volume system and therefore assume that [CF<sub>3</sub>] and [CF<sub>2</sub>] are quite small. The fact that the methyl radical decay rates are not changed when CD<sub>2</sub>H is substituted for CH<sub>3</sub> shows that, even if the NH radical is present in the system, it makes a negligible contribution to the measured decay of the signal at m/e=15. Finally, the only plausible additional reaction of CH<sub>3</sub> is

$$CH_3 + CH_3 \rightarrow C_2H_6.$$
 (5)

Simple modeling calculations show that, with the  $[CH_3]$ , [N] and other conditions of our experiments, decay of  $CH_3$  via reaction (5) makes a negligible contribution to the observed  $CH_3$  decay rate.

The present result may be compared to the estimated value discussed in section 1. Our value of  $k_1 = 8.6 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> at 298 K is four times faster than the value used in the Yung et al. [8] model of the atmosphere of Titan. This discrepancy is not surprising, considering the poor experimental basis upon which the adopted value depended. There is also a value for  $k_1$  obtained by Ha, Paltenghi and Bayes [15] based on computer modeling of CH<sub>3</sub> decays



Fig. 2. Summary plot of corrected pseudo-first-order rate constant  $k_{corr}$  versus the mean nitrogen atom concentration.

observed by photoionization mass spectrometry; the radical was generated in the 193 nm photolysis of CH<sub>3</sub>NO<sub>2</sub> in the presence of N(<sup>4</sup>S). They obtained a value of  $k_1 = (7\pm3) \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> in reasonable agreement with the present work. Our result shows the N+CH<sub>3</sub> reaction to be very rapid indeed with about one collision in two leading to reaction at room temperature. The rate constant  $k(N+CH_3)$  is somewhat greater than that for other N-atom + radical reactions:  $k(N+CH) = 2.1 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> [16] and  $k(N+OH) = 5.0 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> [17]. A similar trend is observed in O-atom+radical reactions:  $k(O+CH_3) = 1.4 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> [1,3,4] is greater than  $k(O+CH) = 9.5 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> [16] and  $k(O+OH) = 3.3 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> [2].

The large rate constant reported here for  $N+CH_3$ supports suggestions that this reaction can be significant in the reaction of active nitrogen with hydrocarbons [5,6] and in the photochemistry of the atmosphere of Titan [7,8]. For quantitative modeling of Titan's atmosphere, the temperature dependence of the rate constant is required. As the next step in the study of the kinetics of the reaction  $N+CH_3$ , we have begun measurements of the rate constant at temperatures above and below 300 K and a full paper will report these measurements in the near future.

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