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D. A. WHYTOCK
J. H. LEE
J. V. MICHAEL
W. A. PAYNE
L. J. STIEF

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GODDARD SPACE FLIGHT CENTER
GREENBELT, MARYLAND

ABSOLUTE RATE OF THE REACTION OF $Cl(^2P)$ WITH METHANE FROM 200-500K

D. A. Whytock*
Department of Chemistry
University of Essex
Colchester, Essex

and

J. H. Lee**, J. V. Michael***, W. A. Payne and L. J. Stief
Astrochemistry Branch
Laboratory for Extraterrestrial Physics
NASA/Goddard Space Flight Center
Greenbelt, Maryland 20771

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*On leave 1975-76 at Catholic University of America, Washington, D.C. 20017

**NAS/NRC Resident Research Associate

***NAS/NRC Senior Resident Research Associate

ABSTRACT

Rate Constants for the reaction of atomic chlorine with methane have been measured from 200-500K using the flash photolysis-resonance fluorescence technique. When the results from fourteen equally spaced experimental determinations are plotted in Arrhenius form a definite curvature is noted. The results are best represented by the least squares equation, $k = (5.44 \pm \overset{16.34}{4.08}) \times 10^{-19}\ T^{(2.50 \pm 0.21)} \exp(-608 \pm 62/T)\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$. The results are compared to previous work and are theoretically discussed.

INTRODUCTION

Rate constants for the reaction of chlorine atoms with hydrogenous species are of great current interest due to the potential importance of such reactions in determining the rate of ozone depletion in the earth's stratosphere[1]. Thus, termination of Cℓ atom chains in the stratosphere can occur via

$$C\ell + RH \rightarrow HC\ell + R \qquad (1)$$

which would result, at least temporarily, in the destruction of Cℓ atoms and interruption of the Cℓ-CℓO chain which destroys ozone. The reaction of Cℓ atoms with CH_4 is of particular importance in this respect because of its abundance in the stratosphere[1].

Until very recently, only three direct studies had been made of the rate constant for the reaction

$$C\ell + CH_4 \rightarrow HC\ell + CH_3 \qquad (2)$$

Davis, Braun and Bass[2] reported a value of $k_2 = (1.5 \pm 0.1) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298K using the flash photolysis-resonance fluorescence (FP-RF) technique. Clyne and Walker[3] measured k_2 using a discharge flow - mass spectrometric (DF-MS) technique and obtained $k_2 = (5.08 \pm 0.53) \times 10^{-11}$ $\exp(-1790 \pm 40/T)$ cm^3 $molecule^{-1}$ s^{-1} from 300-686K, while

Poulet, LeBras and Combourieu[4], using a similar technique, reported $k_2=(1.84\pm0.14) \times 10^{-11} \exp(-1400\pm100/T)$ cm^3 $molecule^{-1}$ s^{-1} from 295-490K. The room temperature values of k_2 from all three studies are in reasonable agreement, but the two temperature dependent studies clearly do not agree.

Very recently several further studies have been performed. Leu and DeMore[5] obtained $k_2=(1.2\pm0.3) \times 10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} at 298K using the DF-MS technique, while the temperature dependence of k_2 has been further studied in several laboratories. Watson, Machado, Fischer and Davis,[6] using the FP-RF technique, obtained $k_2=(7.94\pm0.70) \times 10^{-12}$ $\exp(-1260\pm35/T)$ cm^3 $molecule^{-1}$ s^{-1} from 218-401K. The possibility of non-Arrhenius behaviour of k_2 is clear from the above studies, in that A_2 and E_2 are both higher at higher temperatures, with reasonable agreement on the value of k_2 at room temperature. The possibility of a curved Arrhenius plot was suggested by Manning and Kurylo[7] who obtained $k_2=(7.93\pm1.53) \times 10^{-12} \exp(-1273\pm51/T)$ using FP-RF from 218-322K. However, they noted that their highest and lowest temperature points lay above the Arrhenius line, while the mid-range points lay below the line. Their results from 277-322K could be fitted by the Arrhenius expression $k_2 = (2.77 \pm 1.28) \times 10^{-11} \exp(-1647 \pm 138/T)$ cm^3 $molecule^{-1}$ s^{-1} which was close to that derived from the results of Zahniser and Kaufman[8] from 300-504K. The latter workers measured k_2 from 200-504K using the discharge flow-resonance fluorescence (DF-RF) technique and observed non-linear Arrhenius behaviour.

Much of the apparent discrepancies between the various Arrhenius equations reported for k_2 might be explained if the non-linear Arrhenius behavior obtained by Zahniser and Kaufman were confirmed using an independent technique. To this end, reaction (2) has been studied here at short temperature intervals in the range 200-500K using the FP-RF technique.

EXPERIMENTAL

The FP-RF apparatus used in this study has been described in detail previously.[9] Consequently, only those aspects of the apparatus and procedures which are specific to the study of this reaction will be emphasized here. In all of the reported experiments, chlorine atoms were produced by the flash photolysis of phosgene.[10] Except for one series of experiments at room temperature using a LiF filter, a sapphire filter was used to restrict photolyzing wavelengths to $\lambda \geq 143$ nm so that photolysis of methane in the flash was negligible. Several preliminary experiments at room temperature using a suprasil filter with carbon tetrachloride as the atom source gave results identical to those reported here.

Chlorine atom resonance radiation was produced by flowing a mixture of $C\ell_2$ in He through the microwave discharge resonance lamp. The lamp output was observed with a McPherson Model 218 vacuum monochromator for a variety of compositions and pressure. Optimum conditions were established with 0.1% $C\ell_2$ in He at a pressure of approximately 0.5 torr. The multiplet structure showed only moderate reversal under these operating conditions.[11] Resonantly scattered photons were viewed at right angles through a

BaF_2 filter without wavelength resolution, and the signal was assumed to be linearly proportional to the atom concentration.[12] The 3-component reaction mixtures of methane, phosgene source and argon diluent flowed through the cell at a rate sufficient to replenish the reaction mixture between successive flashes. Preliminary experiments showed that pseudo-first-order rate constants, obtained from exponential decay of the resonance fluorescence, were slightly higher under either static or very slow flow conditions, indicating that secondary complications could contribute at insufficiently fast flow rates.

The pseudo-first-order rate constants obtained in the presence of a large excess of methane were composite since, in addition to reaction with CH_4 and any impurities, $C\ell$ atoms were lost by diffusion out of the reaction viewing zone. The diffusion correction, k_d, was determined independently in the normal way[9] by flash photolyzing mixtures of phosgene and argon at the various experimental temperatures and pressures employed to obtain the kinetic results. At very high incident flash intensities, i.e. at high flash energies and with the optical train from the flash lamp to the reaction cell freshly cleaned, k_d was observed to depend upon the intensity of the flash. Such variations were easily allowed for in practice. The k_d correction term under such conditions never exceeded 10% of the observed decay rate constant and was normally << 10%. For most series of experiments k_d was independent of intensity and was again typically <<10%, although it was ~15% at the highest temperatures studied here.

Argon (Matheson, 99.9995%) and helium (Airco, 99.9999%) were used without further purification. Chlorine (Matheson, 99.5%) was further purified by fractional distillation at 195K and phosgene (Matheson, 99%) was similarly purified by fractionation at 163K. Methane (Matheson, 99.97%) was used without further purification. Gas chromatographic analysis of the CH_4 showed it to contain 32ppm of C_2H_6 as impurity, but no other hydrocarbon impurities were detectable.

RESULTS

Under the pseudo-first-order conditions employed here with $[CH_4] \gg [C\ell]$, the decay of $C\ell$ atoms may be represented by

$$\ell n\, [C\ell] = -k_{observed}\, t + \ell n\, [C\ell]_o \tag{3}$$

where the observed pseudo-first-order rate constant is given by

$$k_{observed} = k_{bi}\, [CH_4] + k_d. \tag{4}$$

Plots of $\ell n\, [C\ell]$ vs t were linear and $k_{observed}$, and hence k_{bi}, was obtained from such plots using a linear least squares analysis. The results are presented in Table 1, and as shown there, k_{bi} was independent of substantial variations in both total pressure and $[CH_4]$. The essential correctness of equation (4) is indicated by the linearity of plots of $k_{observed}$ vs $[CH_4]$, as shown in Fig. 1.

Despite the very high [stable reactant] / [atom] ratios accessible in this system, it has been shown previously[13,14] that contributions from secondary reactions resulting in additional atom loss can become important at very high incident flash intensities i.e., at relatively high atom and/or free radical concentrations. Consequently, the reaction was studied over a wide range of flash intensity, and hence a wide range of $[C\ell]$, under all conditions. For most experimental conditions, the measured k_{bi} was independent of the accessible flash intensity range. However, for some series of experiments, in particular for those performed with a freshly cleaned optical train from flash lamp to reaction cell, the resulting k_{bi} was observed to increase slowly from its low flash energy limit to ~20% above that limit at very high flash energies. This increase in k_{bi} was indicative of secondary complications and, in the few series of experiments where this occurred (at and around room temperature), only those experiments which were clearly independent of a range of intensity are included in Table 1.

In order to obtain k_2 from the k_{bi} values listed in Table 1, corrections to k_{bi} must be applied to account for the fast reaction[7] of $C\ell$ with the 32ppm C_2H_6 impurity always present in the CH_4 used here. Table 1 includes a listing of $k_{bi\ (corrected)}$, the latter being equal to k_2. The correction decreases from ~10% at 200K to ~0.2% at 500K.

Fig. 2 shows an Arrhenius plot of the mean k_2 obtained at each of the 14 temperatures. A linear least squares treatment yields the equation $k_2=(11.0\pm1.2) \times 10^{-12} \exp(-1350\pm30/T)$ cm^3 $molecule^{-1}$ s^{-1}. However, a definite curvature is apparent in Fig. 2. Thus the results may be better represented by an equation of the form $k=AT^n \exp(-B/T)$ and the least squares fit, shown as the dashed line in Fig. 2 is given by the equation $k_2=(5.44^{+16.34}_{-4.08}) \times 10^{-19}\ T^{(2.50\pm0.21)} \exp(-608\pm62/T)\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$.

DISCUSSION

The apparent uncertainty in the Arrhenius parameters for k_2 is evident in the very recent review compiled by Watson.[15] The reported A_2 values range from 5.08×10^{-11} to 7.9×10^{-12} cm^3 $molecule^{-1}$ s^{-1} while the E_2 values range from 3.56 to 2.50 kcal mol^{-1}. It is possible that non-linear Arrhenius behaviour may, at least in part, be responsible for these discrepancies. This has been suggested by Manning and Kurylo[7] and is reinforced by the results obtained here. Thus if the present results are analyzed over temperature ranges equivalent to those used in other studies, as shown in Table 2, the agreement with other studies using resonance fluorescence detection is excellent. The agreement with the DF-MS study of Poulet et al[4] also is good. However this may be fortuitous, given the poor precision of the data from reference (4). The other DF-MS study of Clyne and Walker[3] yields Arrhenius parameters significantly higher than the resonance fluorescence results. Nevertheless, it is clear that much of the apparent conflict in Arrhenius parameters of different studies may be explained by non-linear Arrhenius behavior, with the resulting A_2 and E_2 depending on the T range.

The discrepancy between the DF-MS results, obtained under Cl-rich conditions, and those obtained using resonance fluorescence detection under CH_4-rich conditions, is presented graphically in Fig. 3. The DF-MS results, represented by filled symbols, seem generally ~20% higher than the open symbols of the resonance fluorescence data and in general the two sets of results do not quite overlap within the claimed uncertainties. Nevertheless it is clear from Fig. 3 that the rate constant k_2 is known with a great deal more precision than most gas kinetic rate constants. This is particularly so between 200-300K, since all of the resonance fluorescence results, both DF-RF and FP-RF, are in remarkably good agreement. The present results are essentially identical to those of Manning and Kurylo[7] and lie between the slightly higher values of Watson et al[6] and the slightly lower values of Zahniser and Kaufman.[8]

However, as indicated in Fig. 2 and Table 2, the present results over the complete 200-500K range seem best represented by a 3-parameter fit given by $k_2=(5.44^{+16.34}_{-4.08}) \times 10^{-19}$ $T^{(2.50\pm0.21)} \exp(-608\pm62/T)$ cm^3 $molecule^{-1}$ s^{-1}. All of the resonance fluorescence results from references (2), (6), (7), and (8), together with the present results, can be fitted to the similar expression $k_2=(2.08^{+88.32}_{-2.03}) \times 10^{-17}$

$T^{(1.96\pm0.56)}\exp(-766\pm168/T)$ cm^3 $molecule^{-1}$ s^{-1} for 200-504K. The difference between these two equations is largely a result of the uneven distribution of the combined data over this temperature range, in particular the paucity of data at T>407K.

A theoretical description of reaction (2) has already been reported with the BEBO method in order to explain measured kinetic isotope effects,[16,17] and these calculations included one dimensional tunneling corrections. We have extended the BEBO calculation by including triplet repulsion and using separate values for bond indices.[17] Also one dimensional Eckart tunneling factors have been included after the method of Truhlar and Kuppermann[18] in contrast to that of Johnston.[17,19] The two methyl wags in the activated complex are assumed to be degenerate, and its frequency is taken as a parameter in fitting the data. For a value of 1140 cm^{-1}, the computed values are well represented by $k = 8.4 \times 10^{-19}\ T^{2.5}\exp(-748/T)$ over the temperature range 200-500K.

The agreement between calculated and experimental results is excellent but may be fortuitous given the approximate nature of BEBO and the uncertainties surrounding both the application of one dimensional tunneling theory[19] and the ambiguities of activated complex vibration frequency assignments. These inadequacies are further reflected in isotope effect calculations. Consistent extension of the model to $C\ell + CD_4$ predicts $(k_H/k_D)_{300K} = 20$, whereas the measured value is 11.0.[16] Thus, the experimentally observed non-Arrhenius behavior cannot be used to imply the correctness of the model and, in particular, the presence of tunneling. On the other hand the model as described is consistent with experiment. We point out for the present case that the greatest ambiguities arise from tunneling corrections and vibration frequency assignments and not from the method of obtaining the potential energy of interaction (BEBO). Even with more sophisticated methods (eg. LEPS), the above mentioned ambiguities will still be present and will make the theoretical results somewhat arbitrary.

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Table 1. Rate data for the reaction $Cl + CH_4 \rightarrow HCl + CH_3$

$\frac{T}{K}$	$\frac{P_{Ar}}{Torr}$	$\frac{P_{CH_4}}{mTorr}$	$\frac{P_{COCl_2}}{mTorr}$	$\frac{\text{Flash}^a\ \text{energy}}{J}$	No. of experiments	$\frac{k_{bi}{}^c}{10^{-14}cm^3\ molecule^{-1}\ s^{-1}}$	$\frac{k_{bi}\ (corrected)}{10^{-14}cm^3\ molecule^{-1}s^{-1}}$
500	50	50	75	38-182	15	90.2 ± 8.1	
500	50	65	75	33-144	16	91.4 ± 6.6	
					31	90.8 ± 7.3^d	90.6 ± 7.3^e
447	100	70	75	28-182	12	56.1 ± 4.1	
447	100	100	75	28-203	12	56.6 ± 4.7	
447	200	50	150	44-182	9	59.9 ± 2.0	
					33	57.3 ± 4.1^d	57.1 ± 4.1^e
404	80	53.3	53.3	9-110	15	36.5 ± 3.1	
404	80	160	53.3	9-116	16	39.3 ± 1.6	
					31	37.9 ± 2.8^d	37.7 ± 2.8^e
371	50	100	33.3	18- 46	6	28.2 ± 1.1	
371	100	66.6	66.6	7- 95	13	27.4 ± 1.7	
					19	27.6 ± 1.5^d	27.4 ± 1.5^e
343	35	210	70	28-144	12	21.1 ± 1.6	
343	50	100	100	9- 42	12	20.2 ± 1.1	
					24	20.6 ± 1.4^d	20.4 ± 1.4^e

318	50	100	100	7- 20	7	13.8±0.6	
318	50	300	100	12-144	15	14.0±0.5	
					22	14.0±0.5[d]	13.8±0.5[e]
299	25	50	50	7- 52	13	11.9±0.7	
299	50	50	25	6- 38	13	11.3±0.6	
299	50	50	25	9- 32[b]	8	11.7±0.8	
299	50	100	100	6- 26	18	11.5±0.6	
299	50	300	100	6- 36	11	11.2±0.6	
299	200	200	100	9- 29	8	11.2±0.4	
299	300	400	400	18- 44	4	11.7±0.4	
					75	11.5±0.7[d]	11.3±0.7[e]
276	50	100	100	8- 48	12	7.75±0.62	
276	50	300	100	14- 46	10	7.60±0.57	
					22	7.68±0.59[d]	7.49±0.59[e]
260	15	377	37.5	16-182	21	5.79±0.47	
260	15	564	37.5	16-182	25	5.98±0.41	
					46	5.90±0.44[d]	5.71±0.44[e]
245	15	564	37.5	56-182	8	4.44±0.40	
245	30	754	75	28-182	15	4.16±0.15	
245	30	1129	75	56-182	10	4.38±0.15	
					33	4.29±0.26[d]	4.11±0.26[e]

232	30	754	75	56-144	9	3.31 ± 0.18	
232	30	1129	75	56-182	11	3.50 ± 0.17	
					20	3.41 ± 0.20^d	3.24 ± 0.20^e
220	35	879	87.5	29-182	18	2.47 ± 0.14	
220	35	1317	87.5	29-203	12	2.58 ± 0.21	
					30	2.51 ± 0.18^d	2.34 ± 0.18^e
210	35	879	87.5	50-163	16	2.02 ± 0.13	
210	35	1317	87.5	56-182	12	2.16 ± 0.13	
					28	2.08 ± 0.14^d	1.91 ± 0.14^e
200	40	1005	100	36-182	16	1.61 ± 0.09	
200	40	1505	100	31-182	9	1.68 ± 0.08	
					25	1.63 ± 0.09^d	1.46 ± 0.09^e

a sapphire filter on the flash lamp except where noted.

b LiF filter on the flash lamp.

c uncertainty is one standard deviation.

d mean value of k_{bi} at that temperature.

e mean value of k_{bi} at that temperature, corrected for 32 ppm C_2H_6 impurity.

Table 2. Linear least squares Arrhenius parameters for k_2

T range K	$A_2{}^a$ 10^{-12} cm^3 molecule^{-1} s^{-1}	$E_2{}^a$ kcal mole^{-1}	Reference
218-322	7.93±1.53	2.53±0.10	7
220-318	7.83±0.67	2.54±0.04	this work
218-401	7.94±0.70	2.50±0.07	6
220-404	9.91±0.67	2.66±0.04	this work
200-504	13.6±2.0	2.87±0.08	8
200-500	11.0±1.2	2.69±0.06	this work
296-504	22.5±3.1	3.23±0.08	8
299-500	18.4±2.8	3.07±0.10	this work
296-490	19.2±5.8[b]	2.86±0.19	4
300-484	42.4±14.1[c]	3.42±0.22[c]	3

[a] error limit is the standard deviation.

[b] recalculated from the original data; the author's quoted A-factor and error limit for A appear to be wrongly calculated in ref. 4.

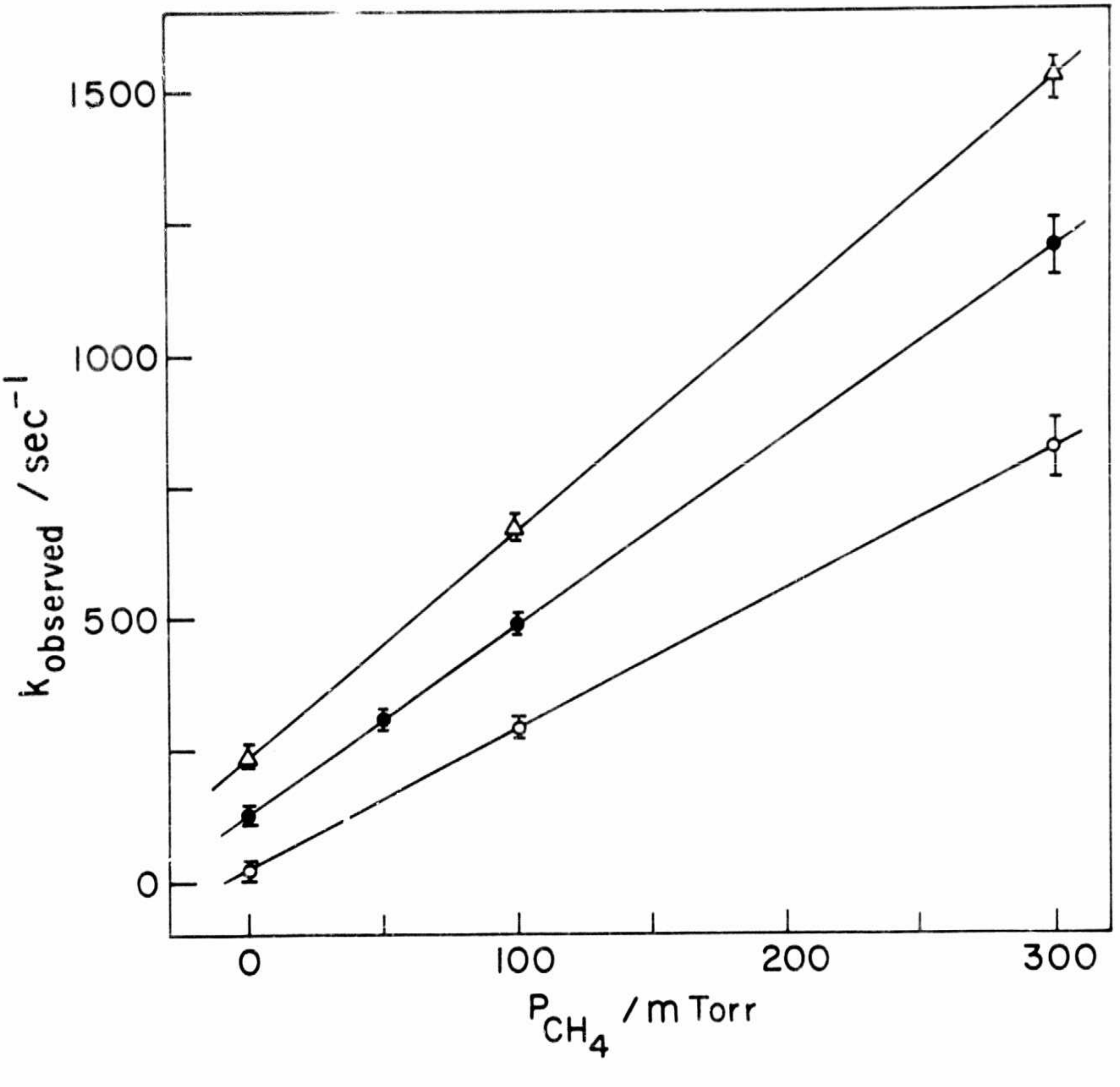
[c] although this study was from 300-686K, these parameters apply only to the data from 300-484K.

FIGURE CAPTIONS

Fig. 1. Pseudo-first-order rate constant $k_{observed}$ vs $[CH_4]$ for the conditions O: 276 K, P_{total} = 50 Torr; ●: 299 K, P_{total} = 50 Torr, and displaced upwards by $100 s^{-1}$; ♦: 318 K, P_{total} = 50 Torr, and displaced upwards by $200 s^{-1}$.

Fig. 2. Plot of $\log_{10} k_2$ (=$\log_{10} k_{bi}$ (corrected) vs $\frac{1}{T}$. The dashed line represents $\log_{10} k_2$ evaluated from the equation $k_2 = 5.44 \times 10^{-19} T^{2.50} \exp(-608/T)$ cm^3 $molecule^{-1}$ s^{-1}.

Fig. 3. Comparison of $\log_{10} k_2$ values; filled symbols represent DF-MS data while open symbols are DF-RF and FP-RF data, as follows: ●, ref. 3; ▼, ref. 5; ▲, ref. 4; ■, ref. 8; ▽, ref. 2; △, ref. 6; ◊, ref. 7; O, this work.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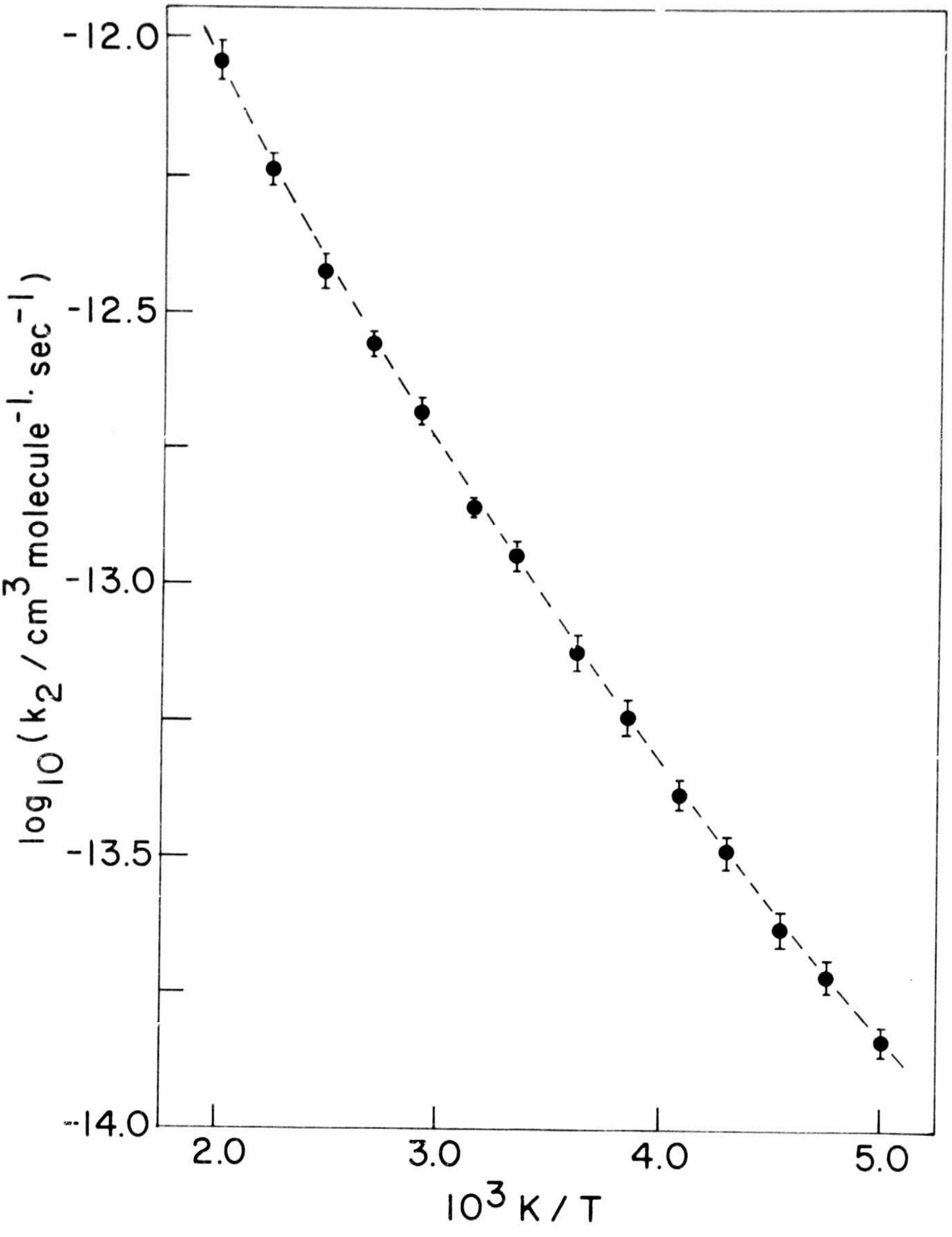
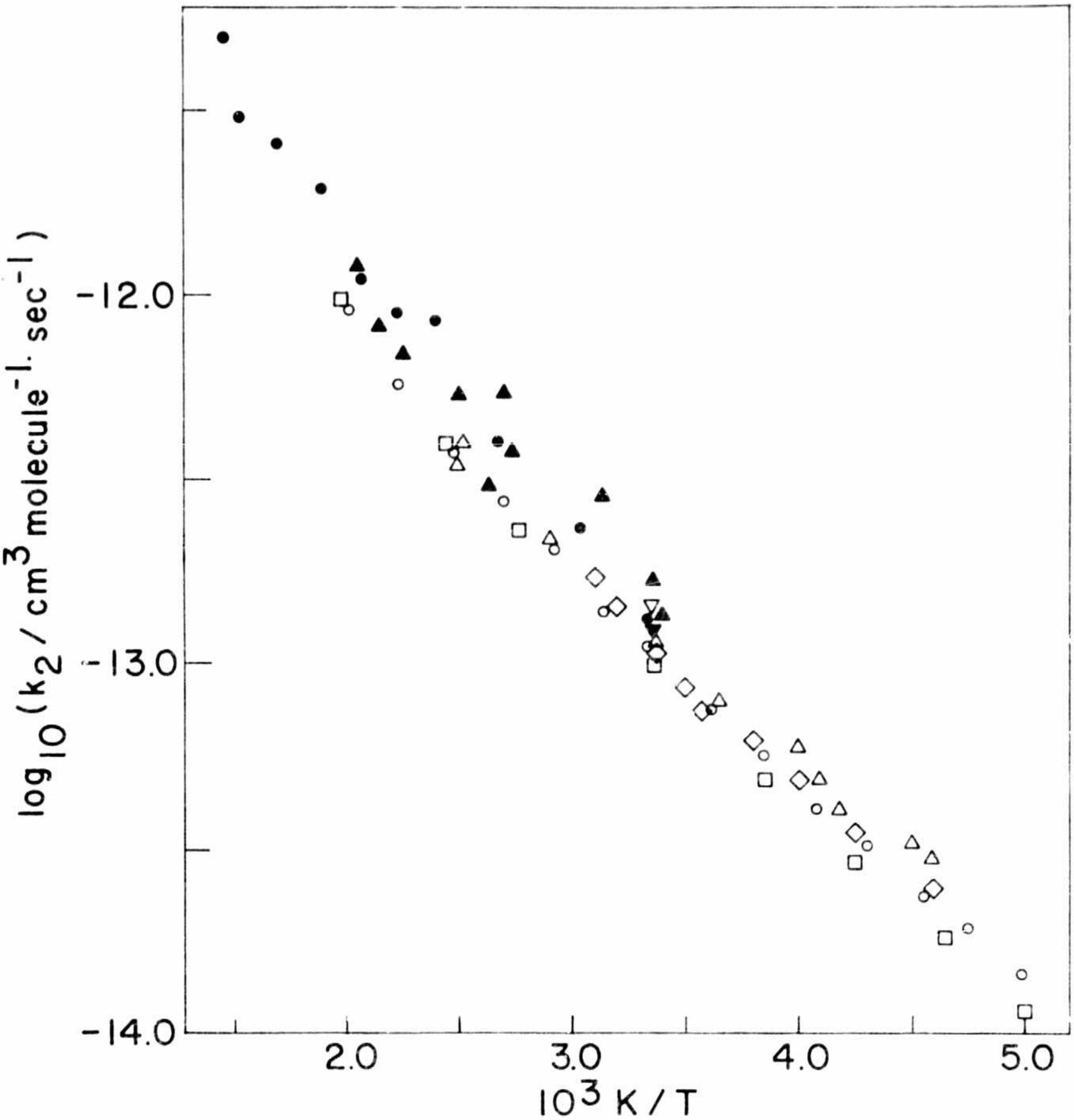
1000
500
0
$k_{observed}$ / sec^{-1}
0
100
200
300
P_{CH_4} / m Torr


-12.0
-12.5
-13.0
-13.5
-14.0
2.0
3.0
4.0
5.0
10^3 K / T
$\log_{10}(k_2/\mathrm{cm}^3\,\mathrm{molecule}^{-1}\cdot\mathrm{sec}^{-1})$



$\log_{10}(k_2 / \text{cm}^3\,\text{molecule}^{-1}\cdot\text{sec}^{-1})$
-12.0
-13.0
-14.0
2.0
3.0
4.0
5.0
$10^3\,K/T$