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AUTHOR(S):
Paul J. Wantuck, CLS-8
Richard C. Oldenborg, CLS-4
Steven L. Baugchum, Spectra Technologies
Kenneth R. Winn, CLS-4

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DIRECT MEASUREMENTS OF METHOXY REMOVAL RATE CONSTANTS FOR COLLISIONS WITH CH_4, Ar, N_2, Xe, AND CF_4 IN THE TEMPERATURE RANGE 673-973K

Paul J. Wantuck, Richard C. Oldenborg, Steven L. Baughcum*,
and Kenneth R. Winn
Chemical and Laser Sciences Division
Los Alamos National Laboratory
Los Alamos, New Mexico 87545

ABSTRACT

Removal rate constants for CH_3O by CH_4, Ar, N_2, Xe, and CF_4 were measured over a 400K temperature range using a laser photolysis/ laser-induced fluorescence technique. Rapid methoxy removal rates are observed for the non-reactive collision partners (Ar, N_2, Xe, and CF_4) at elevated temperatures showing that the dissociation and isomerization channels for CH_3O are indeed important. The total removal rate constant (reaction + dissociation and/or isomerization) for CH_4 exhibits a linear dependence on temperature and has a removal rate constant, k_r = $(1.2\pm0.6)X10^{-8}\exp[(-101070\pm350)/T]$ $cm^3 molecule^{-1} s^{-1}$. Assuming that the removal rate constant due to dissociation and/or isomerization are similar for CH_4 and CF_4, the reaction rate constant for $CH_3O + CH_4$ is equal to $(1.7\pm1.0)X10^{-10}\exp[(-7480\pm1100)/T]$ $cm^3 molecule^{-1} s^{-1}$.

*Present address: Spectra Technology, 2755 Northrup Way, Bellevue, WA 98004

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INTRODUCTION

Methoxy radicals are believed to be important reaction intermediates in the gas phase oxidation of most hydrocarbons. Until quite recently, most information on the reactivity of this radical was based upon indirect kinetic measurements. The lack of detailed reaction rate information for methoxy has made it difficult to ascertain the role of CH_3O in combustion processes and under what conditions the radical is important.

The methoxy radical can react in a variety of ways depending on the identity of the collision partner. In collisions with hydrocarbons a hydrogen abstraction reaction can occur in which the radical extracts an H-atom, e.g.,

$$CH_3O + CH_4 \rightarrow CH_3OH + CH_3 \tag{1}$$

In addition to this reactive channel, collisions with other reactive and non-reactive species can cause dissociation of the methoxy via the reaction

$$CH_3O + M \rightarrow CH_2O + H + M \tag{2}$$

or isomerization,

$$CH_3O + M \rightarrow CH_2OH + M \tag{3}$$

Reaction 1, the hydrogen abstraction reaction, represents a methanol production channel. Removal rate constant data for this reaction is quite limited. Shaw and Thynne[1] determined a rate constant for reaction (1) at

455K to be 1.5×10^{-17} cm^{3}molecule^{-1}s^{-1}. Tsang and Hampson[2] proposed the expression (based upon the measurement of Shaw and Thynne and more current thermodynamic data), $k_1(T) = 2.6 \times 10^{-13}\exp(-4450/T)$ cm^{3}molecule^{-1}s^{-1}, to describe the variation of the rate constant with temperature.

Theoretical studies[3] predict that both the decomposition and isomerization reactions for CH_3O have high and similar activation barriers (34.4 and 36 kcal mol^{-1}, respectively). Thus, contributions to methoxy radical removal by reactions 2 and/or 3 should be increasingly important at higher temperatures and, for any methoxy reaction, thermal decomposition and isomerization represent competitive channels. As illustrated by reaction (1), methanol (a potential future fuel) is a product of the reaction between methoxy and methane. The decomposition and isomerization processes, however, (i.e. $CH_3O + CH_4 \rightarrow CH_2O + H + CH_4$ or $CH_2OH + CH_4$) produce less desirable products. Thus, the relative rates of these competing processes will determine the amount of methanol that is produced.

As with the $CH_3O + CH_4$ reaction, removal rate constant data for reactions (2) and (3) is limited. On the basis of RRKM calculations, Tsang and Hampson[2] suggest $k(T) = 10^{13.81}T^{-6.65}\exp(-16740/T)$ cm^{3}molecule^{-1}s^{-1} for methoxy collision partners N_2 and Ar. For polyatomic species, they derive the following rate constant expression, $k(T) = 10^{12.71}T^{-6.12}\exp(-16660/T)$ cm^{3}molecule^{-1}s^{-1}.

Accurate methoxy decomposition and isomerization removal rate constant data will help ascertain the importance of the radical in combustion type environments. In addition, such data may help explain the observed non-Arrhenius temperature dependence observed in the $CH_3O + O_2$ and CH_3O + CO removal rate constant data[4,5]. We have investigated the removal of CH_3O by collisions with the non-reactive species Ar, N_2, Xe, and CF_4 as a means of assessing the relative importance of reactions (2) and (3) . In addition, we have reinvestigated the $CH_3O + CH_4$ reaction to determine accurate removal rate constants for use at elevated temperatures. In this paper we report our measurements, obtained over the temperature range 673-973K. A laser photolysis/LIF technique was utilized to perform all these experiments.

EXPERIMENTAL SECTION

Methoxy radicals are produced by photolyzing methanol (CH_3OH) with the 193 nm output of an excimer laser (Lamda Physik, EMG 102) operating on ArF. These methoxy radicals are produced in a temperature controlled mixture containing a known concentration of the reactant gas in 25 Torr of argon diluent. The methanol pressure is held at approximately 30 mTorr. The methoxy radical is monitored by laser-induced fluorescence (LIF) using a Nd:YAG laser-pumped dye laser (Quanta Ray). The excitation wavelength used to monitor the radical is 292.8 nm (assigned as the $A^2A_1, \nu'_3 = 4 \leftarrow X^2E, \nu''_3 = 0$).[6] For these experiments, the time history of the CH_3O radical is obtained by recording the LIF signal intensity as a function of increasing time delay between the photolyzing laser pulse and the probe laser pulse. The CH_3O temporal profiles generated with all reactants are well represented by single exponential decays. By analyzing the rate of this decay as a function of the reactant pressure, the removal rate constant for the particular reactant is deduced.

The experiments are conducted in a high temperature cell (HTC) patterned after a design of Felder and coworkers[7]. Briefly, the HTC consists of an alumina ceramic tube which is heated resistively. This alumina core is surrounded by zirconia fiber insulation and the entire assembly is enclosed in a water-cooled vacuum chamber. Cell temperature is monitored with stainless steel sheathed chromel-alumel thermocouple probes. The output of these probes is sent to a Microcon model 823 microprocessor which automatically regulates the heater current. Temperatures in the observation zone can be different from the set point value, particularly at higher temperatures, but are always within 1% of the set point value and held constant to within 1°C.

The precursor methanol is premixed with argon (2% CH_3OH) and enters the HTC through a water-cooled inlet at the bottom of the cell. The CH_4 (99.99%) and the non-reactive gases [Ar (99.995%), Xe (99.995%), N_2 (99.99%), and CF_4 (99.7%)] are obtained commercially and are used without further purification. These gases are introduced into the HTC through an inlet located at the cell base and flow upward with a speed of approximately 5 cm/s. Such a slow flow ensures that a fresh sample of precursor is present for each laser shot yet is essentially static on the timescale of the reaction (<1ms). Cell pressure is measured with a capacitance manometer and gas flows are regulated with calibrated Tylan mass flowmeters.

The excimer and probe laser beams are introduced collinearly into the HTC. The probe laser beam is focused to approximately 0.5 mm diameter while the excimer beam is approximately 3X3 mm at the same location. This arrangement minimizes diffusional mixing effects at the edges of the probe beam. The excimer and dye laser fluences are typically 0.15 and 0.25 J/cm^2, respectively. The broadband methoxy fluorescence emission is imaged through a 305 nm long-pass filter (Schott WG-305) onto the photocathode of a RCA 7265 gated photomultiplier tube. The photomultiplier signal is amplified and sent to a PAR model 162 boxcar signal averager and then recorded and analyzed with an interfaced Data General Nova/Eclipse computer system.

RESULTS and DISCUSSION

Experiments were performed to measure CH_3O + CH_4, Ar, Xe, N_2, and CF_4 removal rate constants as a function of temperature. A typical Stern-Volmer type plot of τ^{-1} vs N_2 pressure at a temperature of 873 K is shown in Figure 1. The slope of line fitted through the data is used to calculate the bimolecular removal rate constant, k_r, for methoxy in the presence of the reactant. The quality of the fit is a good indication of the precision of the measurements and the standard deviation of the slope represents the uncertainty for these measurements. Similar plots were constructed for the other reactant gases at each temperature investigated.

The measured non-reactive, methoxy removal rate constants (for Ar, N_2, Xe, and CF_4) are plotted versus inverse temperature in Figure 2. Rapid methoxy removal rates are observed at the higher temperatures for these collision partners. Clearly, decomposition and/or isomerization are important processes at these temperatures. (We were unable to obtain measurements below 637 K because the removal rates are to slow to measure with the LIF technique.) The solid lines in Figure 2 represent best fits to the Ar, N_2, Xe (these three collision partners are fit to a single expression), and CF_4 data using the empirical Arrhenius expression $k_r(T) = A\exp(-E/RT)$, where A represents the pre-exponential factor, E the activation energy, R the ideal gas constant, and T denotes temperature. For CF_4 in the 673-973 K temperature range, $k_r = (2.4\pm1.5)\mathrm{X}10^{-8}\exp[(-11150\pm480)/T]$ $cm^3molecule^{-1}s^{-1}$, while for Ar, N_2, and Xe, $k_r(T) = (8.1\pm3.6)\mathrm{X}10^{-9}\exp[(-11460\pm302)/T]$ $cm^3molecule^{-1}s^{-1}$. Also shown in Figure 2 is the line corresponding to RRKM based rate constant expressions developed by Tsang and Hampson[2] for the CH_3O + M reaction (M = Ar,N_2 and polyatomics) . Their predicted rate constants agree quite well with our measured values.

The total $CH_3O + CH_4$ removal rate constant is plotted versus inverse temperature in Figure 3. The removal rate constant, like k_r for the non-reactive species, is well represented by a simple Arrhenius expression, and unlike the $CH_3O + O_2$ data[4], no double exponential behavior is observed. The disappearance rate constant for CH_3O by CH_4 is well described by the empirical expression $k(T) = (1.2\pm0.7)\mathrm{X}10^{-8}\exp[(-10170\pm3500)/T]$ $cm^3molecule^{-1}s^{-1}$. The pre-exponential A factor and activation energy are very similar to those obtained for collisions with the non-reactive gases, suggesting that at elevated temperatures, the primary removal process for $CH_3O + CH_4$ is dissociation and/or isomerization. Also shown in Figure 3 is the removal rate constant data for CF_4. The abstraction of a fluorine atom from CF_4, analogous to Reaction (1), is highly endothermic and therefore insignificant. Therefore, assuming that the methoxy removal rate constants due to processes 3 and 4 are similar for CH_4 and CF_4, then the difference between these two curves is due to the abstraction reaction (methanol production) with CH_4. The reaction rate constant calculated in this manner is shown in Figure 4 along with the single value of the reaction rate constant measured by Shaw and Thynne (at 455 K). The line through the data is a least-squares fit of our calculated reaction rate constants combined with this single point. Based on this fit the rate constant for abstraction reaction (1), CH_4 by CH_3O to yield CH_3OH, is $k_1 =$ $(1.7 \pm 1.0) \times 10^{-10} \exp[(-7480 \pm 1100)/T]$ $cm^3 molecule^{-1} s^{-1}$.

Certainly, methoxy removal by dissociation and/or isomerization processes (reactions 2 and 3) is indeed important at elevated temperatures and needs to be considered when evaluating any high temperature methoxy reaction. Methoxy reactions are probably important during ignition processes and in "cool" flame regions, but will decrease in importance as combustion proceeds, the temperature increases, and the decomposition and isomerization channels open up.

We have estimated a reaction rate constant for reaction (1). In contrast to Tsang and Hampsons' recommended value for the reaction rate constant, our results predict a more favorable rate of methanol production with increasing temperature. (We note again that the Tsang and Hampson expression is based upon an extrapolation of the single point measurement of Shaw and Thynne[1] for $CH_30 + CH_4$ using more current thermodynamic data). Our method of correcting the total $CH_3O + CH_4$ removal rate constant is based on the assumption that methoxy removal by CH_4 is an equivalent process to methoxy removal by CF_4. We are currently investigating another method of extracting the reaction rate constant from the total removal rate constant data. A more accurate estimate will be obtained if the collision-induced unimolecular rate constant for processes (2) and/or (3) can be reasonably estimated. Our approach is to use an RRKM formalism to scale our measured removal rate data for the non-reactive collision partners Ar, N_2, Xe, and CF_4 and if successful, extend this scaling to CH_4. As was done with the CF_4 data, the unimolecular rate constant is subtracted from the measured total removal rate constant yielding the reaction rate constant. Preliminary calculations based on this approach are encouraging, however, further analysis is required to fully deconvolute the rate constant for tne $CH_3O + CH_4$ reaction.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

Figure 1. Stern-Volmer plot of the inverse first-order decay constant, τ^{-1}, vs N_2 pressure (T=873 K, P_{Ar} = 25 Torr).

Figure 2. Arrhenius plot of CH_3O + (Ar, N_2, Xe), and CF_4 removal rate constants. Error bars where not shown are smaller than the plot symbol.

Figure 3. Arrhenius plot of CH_3O + CH_4 and CF_4 removal rate constants. Error bars where not shown are smaller than the plot symbol.

Figure 4. Arrhenius plot of the calculated CH_3O + CH_4 reaction rate constant.

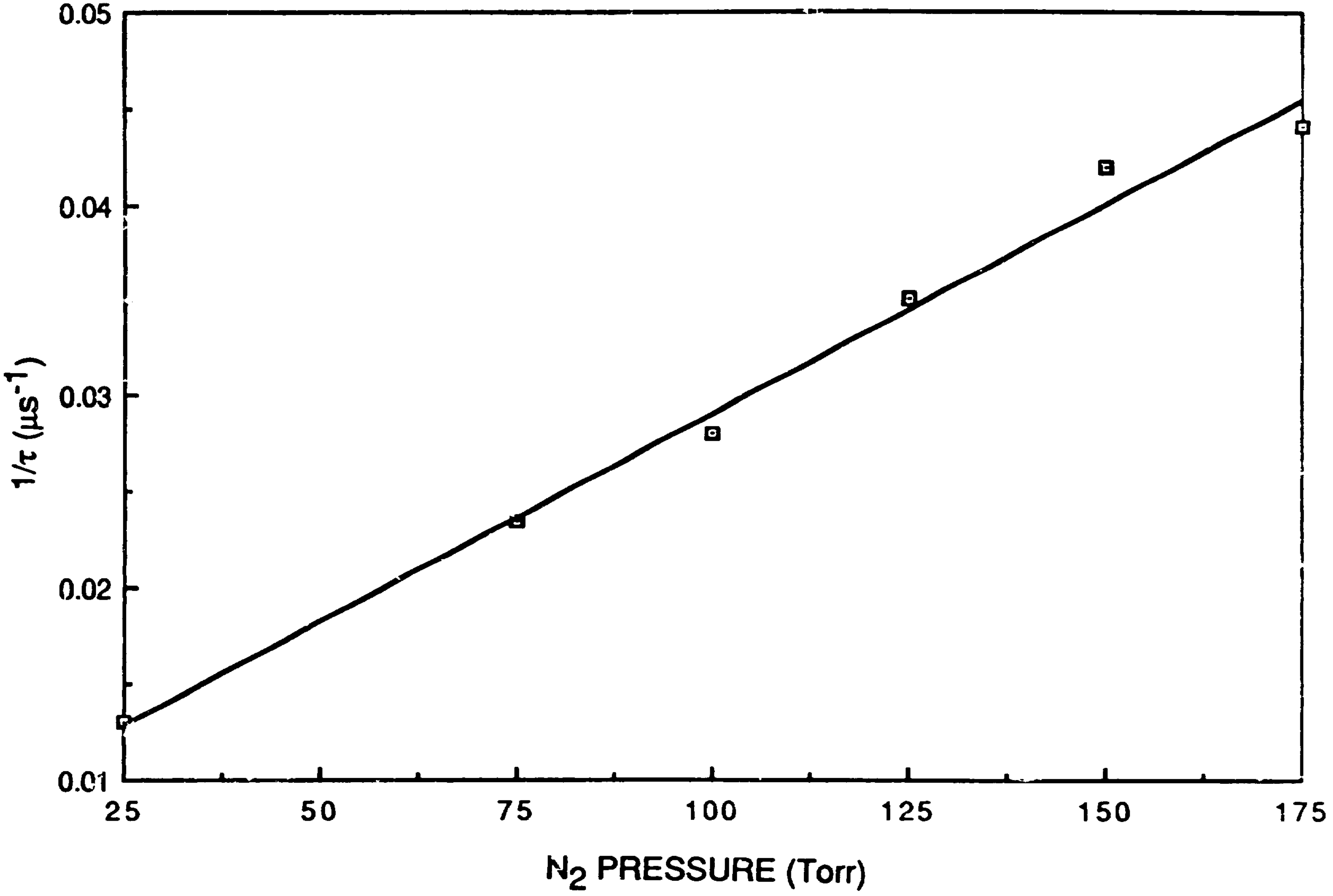
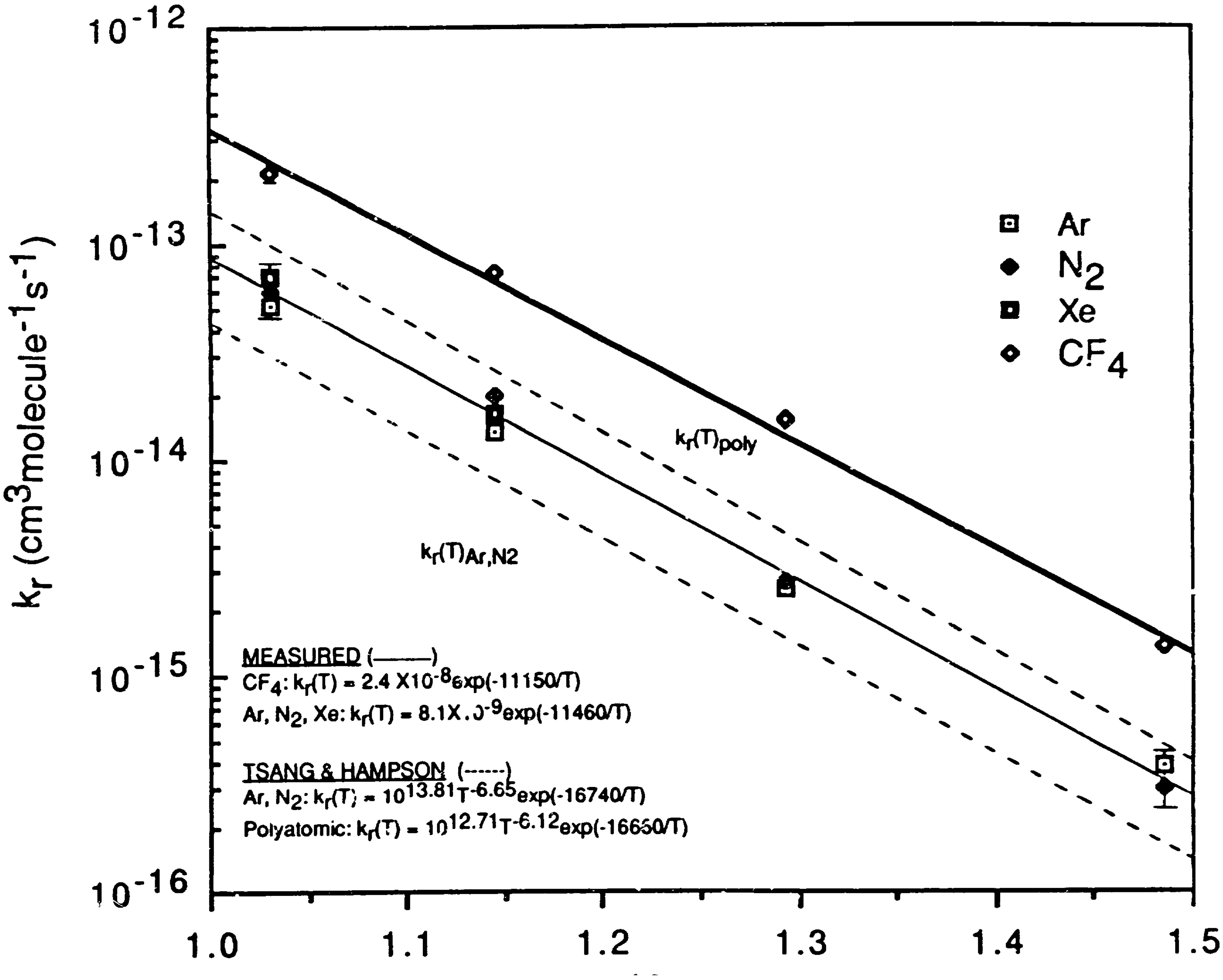

0.05
0.04
0.03
0.02
0.01
1/τ (μs⁻¹)
25
50
75
100
125
150
175
N₂ PRESSURE (Torr)

Figure 1

Figure 2


10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
k_r (cm^{3}molecule^{-1}s^{-1})
1.0
1.1
1.2
1.3
1.4
1.5
Ar
N_2
Xe
CF_4
$k_r(T)_{poly}$
$k_r(T)_{Ar,N2}$
MEASURED (——)
CF_4: $k_r(T) = 2.4 \times 10^{-8} \exp(-11150/T)$
Ar, N_2, Xe: $k_r(T) = 8.1 \times 10^{-9} \exp(-11460/T)$
TSANG & HAMPSON (------)
Ar, N_2: $k_r(T) = 10^{13.81} T^{-6.65} \exp(-16740/T)$
Polyatomic: $k_r(T) = 10^{12.71} T^{-6.12} \exp(-16650/T)$

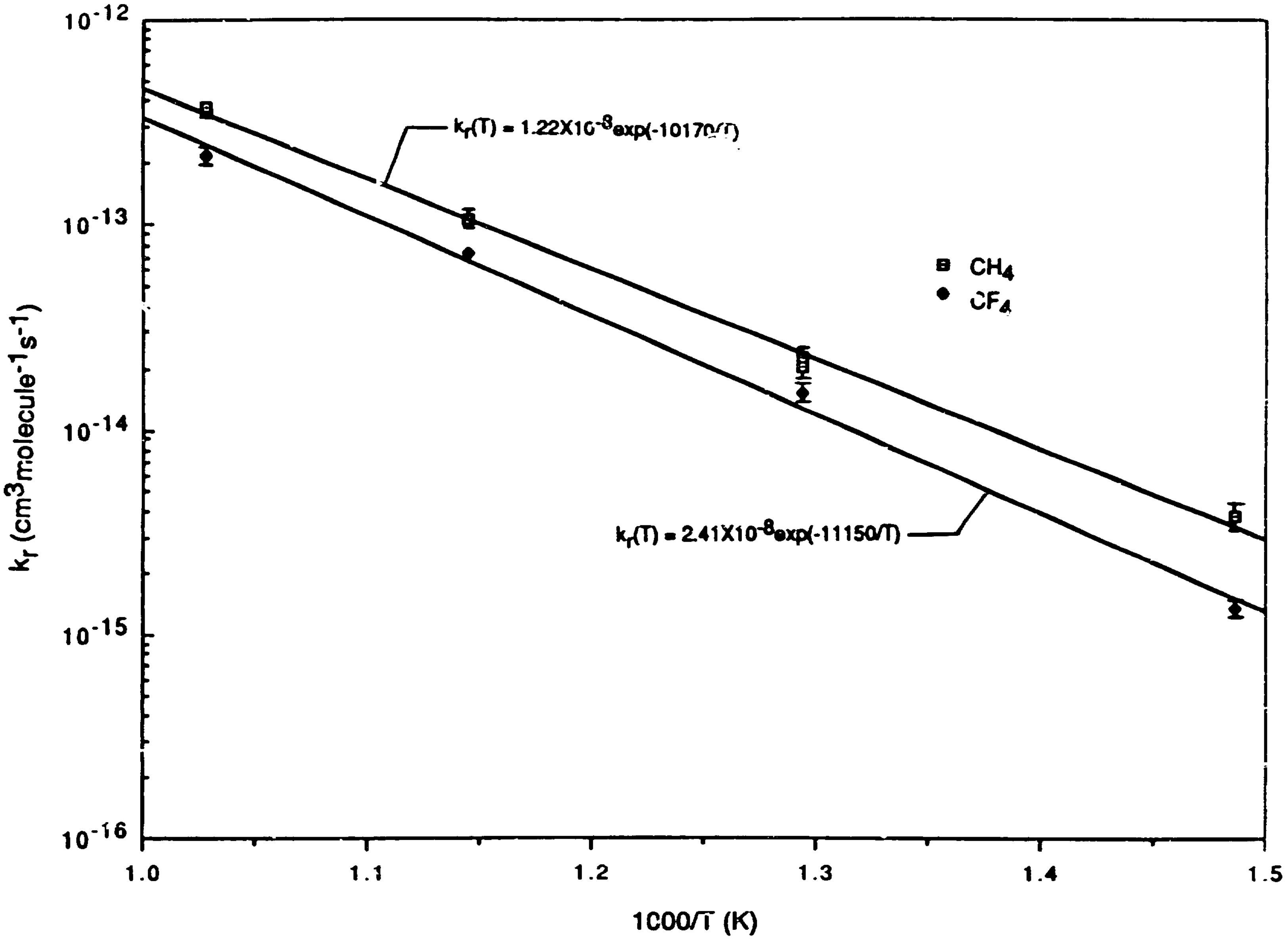
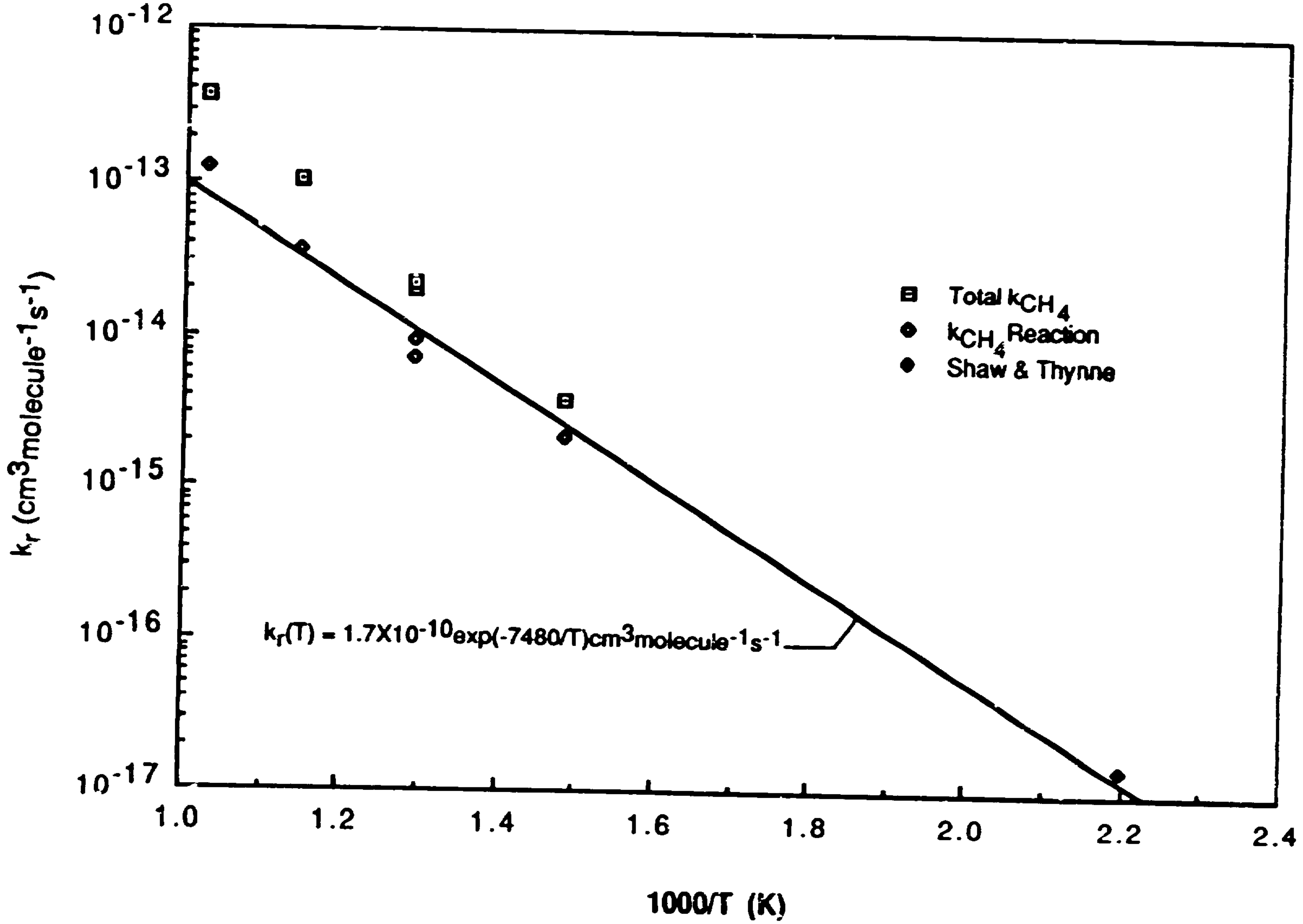

10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
k_r (cm^3molecule^{-1}s^{-1})
$k_r(T) = 1.22X10^{-8}exp(-10170/T)$
$k_r(T) = 2.41X10^{-8}exp(-11150/T)$
CH_4
CF_4
1.0
1.1
1.2
1.3
1.4
1.5
1000/T (K)

Figure 3



10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
k_r ($cm^3 molecule^{-1} s^{-1}$)
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
1000/T (K)
⊡ Total k_{CH_4}
◇ k_{CH_4} Reaction
◆ Shaw & Thynne
$k_r(T) = 1.7X10^{-10} exp(-7480/T) cm^3 molecule^{-1} s^{-1}$