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A KINETICS STUDY OF THE $O(^3P)$ + CH_3Cl REACTION OVER THE 556–1485 K RANGE BY THE HTP AND LP–ST TECHNIQUES

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The high–temperature photochemistry (HTP) and laser photolysis–shock tube (LP–ST) techniques have been combined to study the kinetics of the reaction between ground–state oxygen atoms with CH_3Cl over the temperature range, 556–1485 K. In the HTP reactor, used for the 556–1291 K range, O atoms were generated by flash photolysis of O_2, CO_2 or SO_2, and the atom concentrations were monitored by resonance fluorescence, while with the LP–ST technique, used for the 916–1485 K range, O atoms were generated by the photolysis of either SO_2 or NO with the 193 nm light from a pulsed ArF excimer laser, and atomic resonance absorption spectroscopy (ARAS) was used to monitor $[O]_t$. In both studies, rate coefficients were derived from the [O] profiles under the pseudo–first–order condition, $[O] \ll [CH_3Cl]$. The data obtained by the two techniques are in excellent agreement and are best represented by the expression, $k(T) = 2.57 \times 10^{-11} (T/K)^{0.31} \exp(-5633\ K/T)\ cm^3\ molecule^{-1}\ s^{-1}$ with a 2σ precision varying from ±6 to ±22% and an estimated 2σ accuracy of ±21% to ±30%, depending on temperature. The rate coefficients for the title reaction are essentially identical to those for the O + CH_4 reaction over the observed temperature range, the reasons for which are discussed.

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Introduction

Detailed chemical kinetic models for the combustion of municipal solid wastes and hazardous wastes are needed to improve the understanding of formation and destruction of toxic substances such as chlorinated hydrocarbons.[1] Such models should be based on accurate rate parameters for the elementary reactions that govern the behavior of those combustion processes. However, kinetic information in the approximately 700 to 1600 K range of prime interest[2,3] is largely unavailable. As the first in a series of studies to provide data for those temperatures, we present here observations on the reaction

$$O + CH_3Cl \rightarrow \text{products} \qquad (1)$$

over a very wide temperature range. This is achieved by combining results obtained from the high–temperature photochemistry (HTP) technique[4–8] at Rensselaer and the laser photolysis–shock tube (LP–ST) technique[9,10] at Argonne. Reaction (1) is also important in the chlorine–catalyzed oxidative pyrolysis of methane to form acetylene and ethylene.[11] Previous investigations of reaction (1) include two sets of relative measurements and one set of direct measurements. Wilson and O'Donovan[12] used a discharge flow–mass spectrometer technique from 353 to 949 K to obtain k_1–values relative to the rate coefficients for the O + CH_4 reaction. Westenberg and deHaas[13] used a similar technique, but used O + CH_3Br as the reference reaction. The latter investigation covered the 511–1000 K range. In apparently the only set of direct measurements on this reaction, Barassin and Combourieu[14] measured k_1 in the 298–443 K range using a discharge–flow reactor with mass spectrometric detection. That study monitored [CH_3Cl] under conditions where [O]>>[CH_3Cl], therefore, if CH_3Cl was not regenerated in the flow tube, the results should have been free from stoichiometric complications due to secondary reactions. However, the final rate coefficient inferences depend on a precise knowledge of [O] with that mode of operation.

Experimental

The present study was undertaken to provide a set of direct measurements over a wide temperature range and to allow a direct comparison between results from the two experimental techniques, HTP and LP–ST. In the paragraphs that follow, each technique will in turn be briefly described and details will be discussed that are specific to the present study.

a) High–Temperature Photochemistry (HTP)

The HTP technique and the current operating procedures have been summarized recently.[4–7] The apparatus used is of the design described in an earlier symposium[8] and consists of a 5.1 cm i.d. alumina reaction tube surrounded by helical SiC heating elements and insulation material in a water–cooled stainless–steel vacuum chamber. Reaction gases flow through a moveable cooled–inlet, used to minimize thermal decomposition. The gases emerging from the cooled–inlet are mixed with heated Ar bath gas that is introduced at the upstream end of the reactor. The residence time for mixing, defined by the distance from the tip of the cooled–inlet to the center of the reaction zone divided by the bulk gas velocity, is such that the reaction gases and the bath gas are mixed[4–6] to better than 95% prior to reaching the reaction zone. The reaction zone is defined by the intersection of the fields–of–view of the flash lamp, the cw microwave–discharge flow lamp, and the photomultiplier tube (PMT). Temperature is measured by a Pt–13% Rh/Pt thermocouple, doubly shielded to minimize radiation heat transfer effects. In order to allow correction of any significant temperature gradient near the reaction zone, temperatures 2.5 cm up–, and down–stream of the center of the reaction zone are monitored using chromel–alumel thermocouples.[5] These thermocouples also serve as a ready check on the performance of the main thermocouple. Pressures are measured using an MKS Baratron pressure transducer and gas flow rates are controlled using Teledyne–Hastings mass flow meters and controllers.

In the present study, ground–state oxygen atoms were generated by the flash photolysis of O_2, CO_2, or SO_2 through either MgF_2 (λ>110nm) or Suprasil quartz (λ>165nm) windows. The relative concentrations of the $O(^3P)$ atoms were monitored by fluorescence of the 130.2–130.6 nm resonance triplet, induced by a cw microwave–discharge flow lamp. The lamp contained 2.0 mbar

of flowing 99.999% He. The O–atom fluorescence was detected by the PMT through a CaF_2 (λ>125 nm) window. The use of CaF_2 eliminated the detection of any 121.6 nm H–atom fluorescence. The experiments were carried out under the pseudo–first–order condition, [O]<<[CH_3Cl]; i. e., [O] should decrease exponentially. The pseudo–first–order decay constants, k_{ps1}, were obtained by fitting the fluorescence profiles using the KPS1 routine[15] and included a two–stage residual analysis[7] to ensure that the fluorescence profiles were indeed exponential. Rate coefficient values were then obtained from linear fits of five or six k_{ps1} vs. [CH_3Cl] values at any given set of conditions. The gases used were O_2 (99.6%), CO_2 (99.999%), pure CH_3Cl (99.95%), and 1.01% CH_3Cl in Ar (99.998%) from Matheson, and SO_2 (99.98%), and pure CH_3Cl (99.95%) from Linde.

b) Laser Photolysis–Shock Tube (LP–ST)

The LP–ST technique has already been described in detail[9,10,16] and the methods used in this work have been presented in earlier symposia.[17,18] This apparatus consists of a 7 m (o.d. 4") stainless steel tube separated from a driver section by a thin aluminum diaphragm (4 mil). The tube is routinely pumped to <10^{-8} mbar between experiments. Shock velocities are measured by equally spaced fast pressure transducers, and the thermodynamic conditions in the reflected shock regime are calculated from the incident shock Mach number.[19–21] A Questek 2860 ArF excimer laser supplies a pulse that enters the tube axially through a Suprasil quartz window on the end–plate. This pulse (193 nm, ~25 ns) initiates photolysis in the reflected shock regime. In order to detect the transient species in the hot gas region, an atomic resonance absorption spectroscopy (ARAS) photometer system consisting of an atomic resonance lamp and a solar blind PMT is located 6 cm from the end–plate. Optical access is accomplished with MgF_2 lenses that are mounted directly on the tube. Signals from both the pressure transducers and the PMT are simultaneously recorded by a dual–channel digital oscilloscope.

Experiments are performed in the reflected shock wave regime where the gas is effectively stagnant. The reactant gas mixture is predominantly Ar with small quantities of CH_3Cl accurately measured (MKS Baratron) as the reactant molecule, and either SO_2 or NO added as the photolyte

molecule. He is used as driver gas. Photolysis occurs after the reflected wave has cleared the ARAS photometer position. Laser fluence is controlled by placing wire screens in the path of the beam. This allows for adjustment of $[O]_o$, the initial [O], and therefore minimizes the effects of secondary reactions perturbing the O–atom concentration profile.

O–atom concentration is measured by ARAS. A microwave–driven discharge lamp is the source of the resonance radiation. The lamp is filled with 0.1% O_2 in He and is operated at 40 W and 1.5 mbar. This configuration is similar to that used by Pamidimukkala et al.[22] As in the HTP apparatus, the ARAS signal is filtered through a CaF_2 window in order to exclude H–atom resonance radiation. Also, since some non–resonant radiation is present in the lamp, an atomic filter section is placed in front of the lamp in order to determine the fraction of the signal that is due to the 130.2–130.6 nm triplet. This filter section is a fast discharge–flow system containing 0.3 mbar O_2, which yields sufficient O–atoms in the optical path to absorb all resonance radiation. This filter section measurement is made before each experiment. It is then turned off during kinetic runs.

Absorbance, defined as $(ABS)_t = -\ln(I_t/I_o)$, where I_t and I_o are measured transmitted and initial O–atom resonance lamp intensities, respectively, is determined in the experiment. Since Beer's law holds at low absorbance[22] and $[O] << [CH_3Cl]$, a plot of $\ln(ABS)_t$ vs. time will yield the first–order–decay constant, k_{ps1}, for O–atom removal due to reaction (1). Dividing k_{ps1} by $[CH_3Cl]$ gives a value of k_1 at the conditions of high temperature and density calculated from the incident shock strength.[19-21]

The high purity He (99.995%) used as the driver gas was obtained from Air Products and Chemicals, Inc. The ultra–high purity grade He (99.999%) and extra–dry grade O_2 (99.6%) used in the resonance lamp were from Airco Industrial Gases and Air Products and Chemicals, Inc., respectively. The diluent gas Ar (scientific grade, 99.9999%) was obtained from MG Industries. The reactant molecule, CH_3Cl (99.5%), was obtained from AGA Specialty Gases. The photolyte molecules, SO_2 (anhydrous, 99.98%) and NO (technical grade), were obtained from Matheson Gas Products. CH_3Cl, SO_2, and NO were all subjected to bulb–to–bulb vacuum distillation,

retaining only the middle third, before use. Mass spectrometric analysis of the purified CH_3Cl indicated <0.2% of higher mass chlorinated hydrocarbons.

Results

k_1 measurements were made in the 556 to 1291 K temperature range using the HTP technique. In order to guard against systematic errors, the following wide ranges of experimental parameters were used: pressure P, 130 to 710 mbar; total gas concentrations [M], 1.10×10^{18} to 7.70×10^{18} cm^{-3}; flash energy F, 2.2 to 25 J; bulk gas velocity v, 8.1 to 27 cm s^{-1}; distance from the tip of the cooled–inlet to the reaction zone z, 5 to 47 cm. Moreover, oxygen atoms were generated by photolysis of O_2 through either MgF_2 or Suprasil quartz filters, of CO_2 through MgF_2, or of SO_2 through Suprasil quartz. Also as a safeguard, three different cylinders of CH_3Cl from two different suppliers (see above) were used in the kinetic runs. Within the scatter of the data, no dependence of the measured rate coefficient values on these factors was observed, which indicates that i) any complication from reaction products or photofragments of CH_3Cl was negligible and ii) the errors arising from any impurities in the gases used were small.

In the HTP work, several k_1 measurements were carried out in the 330–510 K range,[23] and comparison with the measurements of Wilson and O'Donovan,[12] Westenberg and deHaas,[13] and Barassin and Combourieu[14] showed that, at around 400 K, the HTP data are somewhat lower. At the lowest temperature investigated, 300 K, all four data sets agree well. A careful examination of all databases suggests a distinct leveling off of k_1 with decreasing temperature. The present HTP data are not reported here partly because our quantum–mechanical tunneling calculations,[23] based on a one–dimensional Eckart barrier, could not reproduce the observed curvature, even though similar calculations have reproduced the data in several earlier H–atom transfer studies quite well.[4,5,24] The explanation for this behavior might lie in the influence of secondary reactions similar to the observations of Westenberg and deHaas on the O + CH_4 reaction.[25] Therefore, in the present work the effects of secondary reactions on the O–atom profiles had to be carefully considered. The mechanism used in modeling calculations included reaction (1), as well as

$$O + CH_2Cl \rightarrow CH_2O + Cl \quad (2)$$

$$O + OH \rightarrow O_2 + H \quad (3)$$

$$OH + CH_3Cl \rightarrow H_2O + CH_2Cl \quad (4)$$

$$OH + OH \rightarrow H_2O + O \quad (5)$$

$$H + CH_3Cl \rightarrow H_2 + CH_2Cl \quad (6)$$

$$Cl + CH_3Cl \rightarrow HCl + CH_2Cl \quad (7)$$

$$O + CH_3 \rightarrow CH_2O + H \quad (8)$$

The modeling study was performed with the Acuchem program.[26] Rate coefficients were taken from Warnatz[27] and/or the NASA compilation.[28] Using the estimated $[O]_o$, $[CH_3]_o$, and $[Cl]_o$ of about $1x10^{11}$ cm^{-3}, from $CH_3Cl+h\nu \rightarrow CH_3+Cl$, rate coefficient values for reaction (1) were generated by plotting O–atom first–order decay constants vs. $[CH_3Cl]$, where the decay constants were obtained by the Acuchem calculation. The k_1–values obtained were greater than the input values by factors of 2.67 and 1.34 at 370 and 410 K, respectively, showing the great importance of the fast processes, reactions (2) and (8), both of which were taken to have identical rate coefficients, i.e. $1.2x10^{-10}$ cm^3 $molecule^{-1}$ s^{-1}. Above 530 K, the calculated values are, within experimental error, identical to the input values. For that reason, data obtained below 530 K are not included in the k_1 recommendation. The data are shown in Fig.1, and an extended table that includes details of the experimental conditions is available from A. Fontijn upon request.

Over the range 556–1291 K, the thirty–five rate coefficient values from the HTP study can be represented by the Arrhenius equation, k(T)=A exp(–B K/T),

$$k_1(T) = 3.26 \times 10^{-10} \exp(-5973\ K/T)\ cm^3\ molecule^{-1}\ s^{-1} \quad (I)$$

for which the variances and the covariance are $\sigma_A^2=5.81x10^{-2}$ A^2, $\sigma_B^2=4.04x10^4$, and $\sigma_{AB}=47.8$ A. These values yield 2σ precision limits varying from ±12 to ±28%. The line

calculated from equation (I) is shown in Fig.1. Compared to the previous determinations[12–14] of k_1, the present data are somewhat lower in the 560 to about 800 K range. It should be noted that the present rate coefficient determinations are absolute, while those of Wilson and O'Donovan[12] and Westenberg and deHaas[13] are based on relative measurements. Nevertheless, as a further check on the accuracy of the present HTP data set, a few rate coefficient measurements on the O + C_2H_4 reaction in the 450–950 K range have been made during the course of the O + CH_3Cl study. These values show good agreement with a recent recommendation of Klemm et al.,[29] derived from several sets of data. Thus, the present HTP technique appears to be free of systematic errors.

For the LP–ST results, similar modeling calculations were performed with reactions (1) – (8). However, one additional process had to be included in the mechanism,

$$CH_3Cl\ (+M) \rightarrow CH_3 + Cl\ (+M) \qquad (9)$$

(The onset of this reaction also determined the upper temperature limit of the HTP study.) Rate coefficients for reaction (9) have been reported by Kondo et al.[30] LP–ST modeling calculations showed that this thermal decomposition was fast enough at high temperatures to give substantial [CH_3], and, because of reaction (8), this resulted in a larger O–atom decay than expected from the product $k_1[CH_3Cl]$. This caused the experimentally observed rate coefficients to rise quite rapidly in the 1500 to 1700 K range. Because of this reaction, k_1–values could not even be measured above 1700 K. Since this perturbation exists, we decided to eliminate the results of all experiment above 1500 K.

Even though the decay constants are typically about a factor of ten higher with the LP–ST technique than in the HTP work, thereby suggesting that secondary reactions are not as important, it should be realized that the initial [O] values are substantially higher in this single shot experiment. Calibration experiments with N_2O dissociation showed that $[O]_0$ was between 3 and 10×10^{12} cm^{-3} for the reported experiments. Hence, perturbation mostly by reaction (2) could be substantial depending on initial conditions. We modeled all experiments and eliminated all values

where stoichiometric factors were greater than 1.24 since the data scatter is about ±24%. These factors were assessed by calculating the apparent O–atom first–order decay constant from the modeled experiment and dividing this value by the input value, $k_1[CH_3Cl]$. The final values reported in Fig.2 are not corrected for stoichiometry because the factor is less than the two standard deviation value at any T, namely, ±24% (see below). An extended table that includes details of the experimental conditions is available from J. V. Michael on request.

While there may be curvature in the ln k(T) vs. T^{-1} plot shown in Fig.2, we have fitted the LP–ST data also by the Arrhenius equation, k(T)=A exp(–B K/T),

$$k_1(T) = 4.82 \times 10^{-10} \exp(-6574\ K/T)\ cm^3\ molecule^{-1}\ s^{-1} \qquad (II)$$

over the temperature range, 916–1485 K. The variances and the covariance for the parameters are σ_A^2=8.62x10^{-2} A^2, σ_B^2=1.40x10^5, and σ_{AB}=1.09x10^2 A, which yield 2σ precision limits of ±6 to ±24% depending on temperature. The line calculated from equation (II) is shown in Fig.2, and the maximum two standard deviation of the points from the equation is ±24%.

It should be noted that the two determinations are in excellent agreement, within combined errors, over the common range of temperature overlap with equation (I) giving 4.80x10^{-13} and 3.19x10^{-12} and equation (II) giving 3.68x10^{-13} and 2.96x10^{-12}, all in units of cm^3 $molecule^{-1}$ s^{-1}, at 916 and 1291 K, respectively; i. e., the results are within ±4 to ±13% of the average over this temperature range. There are apparently no higher temperature data available in the literature for comparison to the LP–ST data.

Both sets of data are combined in Fig.3. A fit to the three parameter equation, k(T) = A $(T/K)^n$ exp(–B K/T), of the combined data yields

$$k_1(T) = 2.57 \times 10^{-11} (T/K)^{0.31} \exp(-5633\ K/T)\ cm^3\ molecule^{-1}\ s^{-1} \qquad (III)$$

for the combined temperature range, 556 to 1485 K. The variances and the covariances are σ_A^2=2.81x10^{-2} A^2, σ_n^2=–2.00x10^{-4}, σ_B^2=9.29x10^3, σ_{An}=3.24x10^{-3} A, σ_{AB}=–3.00 A, and σ_{nB}=1.58. While the 2σ precision limits of the data vary from ±6 to ±22%, we allow ±20% for any possible systematic errors and recommend 2σ accuracy limits to be in the ±21 to ±30% range. For comparison with the combined data, the line calculated from equation (III) is shown in Fig.3. We also show in Fig.3 values from two of the earlier lower temperature studies.[12,13]

Discussion

A priori, two spin–allowed reaction channels can be written for the title reaction,

$$O + CH_3Cl \rightarrow OH + CH_2Cl \qquad (1a)$$

$$O + CH_3Cl \rightarrow OCl + CH_3 \qquad (1b)$$

for which the heats of reaction at 298 K are found[31] to be –6.0 and 84.7 kJ mol^{-1}, respectively. These channels have been considered by Wilson and O'Donovan.[12] In view of their observed activation energy of 35.4 kJ mol^{-1}, which is lower than the estimated ΔH^o_{298K} for channel (1b), they concluded that channel (1a) is the dominant channel, with (1b) being negligible for their investigated temperature range of 353–949 K. From equations (I) and/or (II), the apparent activation energy is 50 to 55 kJ mol^{-1} and therefore less than the endoergicity of reaction (1b). Hence, the present results suggest that reaction (1b) is negligible over the present temperature range as well.

It is interesting to compare the title reaction with the O+CH_4 reaction, for which ΔH^o_{298K} is 10.4 kJ mol^{-1}.[31] Sutherland, Michael, and Klemm[32] have fitted their flash photolysis–shock tube results below 1600 K to a simple Arrhenius expression and have shown that the resulting expression is in good agreement with other lower temperature results.[25,33,34] They reported,

$$k_{O+CH4} = (2.09 \pm 0.20) \times 10^{-10} \exp(-5521 \pm 105\ K/T)\ cm^3\ molecule^{-1}\ s^{-1} \qquad (IV)$$

The ratios of equation (III) to (IV) at 560, 1000, and 1500 K are 0.72, 0.94, and 1.10, respectively, showing that both reactions exhibit the same rate behavior within experimental error over this extended temperature range.

The closeness of the results between $O+CH_3Cl$ and CH_4 may seem surprising since the ΔH^o_{298K} values, –6.0 and 10.4 kJ mol^{-1}, respectively, are so different. In a BEBO theoretical calculation of O–atom abstractions,[35] the potential barrier for the methane reaction was found to be 45.2 kJ mol^{-1}. This can be compared to the $O+C_2H_6$ reaction where the barrier height was 32.5 kJ mol^{-1},[35] even though that reaction is exothermic at $\Delta H^o_{298K} = -16.7$ kJ mol^{-1}. Thus, the reaction (1) case is seen to be intermediate between the two cases suggesting that the C–H bond strength in CH_3Cl is somewhat higher than in ethane but is lower than in methane. This relationship is further corroborated by considering the relative rate behavior of Cl–atom abstractions for the three cases.[28] The apparent activation energy for the $Cl+CH_3Cl$ reaction lies between the values for $Cl+CH_4$ and C_2H_6, showing again that the case is intermediate. A theoretical model for the $O+CH_3Cl$ reaction of the type presented earlier[35] would give a barrier height of about 40 kJ mol^{-1}. Hence, one would expect a larger Boltzmann factor due to the lower barrier height, but this would be offset by a decreased path degeneracy in the A–factor. The end result of combining both factors is to give values that are not much different than in the $O+CH_4$ reaction.

Conclusions

Rate coefficients measured by two techniques are reported for the $O+CH_3Cl$ reaction over an extended temperature range. The results show that the rate behavior is quite similar to that of the $O+CH_4$ reaction. This similarity and thermochemical arguments strongly suggest that the reaction is a simple metathetical abstraction reaction forming OH–, and CH_2Cl–radicals as the reaction products. The rate behavior and reaction product information are important in assessing

chemical models for designing strategies for chlorinated hydrocarbon disposal by combustion techniques.

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Figure Captions

Figure 1 Summary of the HTP rate coefficient measurements for the $O+CH_3Cl$ reaction:

(———) best–fit, eq.(I)

Figure 2 Summary of the LP–ST rate coefficient measurements for the $O+CH_3Cl$ reaction:

(———) best–fit, eq.(II)

Figure 3 Comparison of rate coefficient measurements for the $O+CH_3Cl$ reaction:

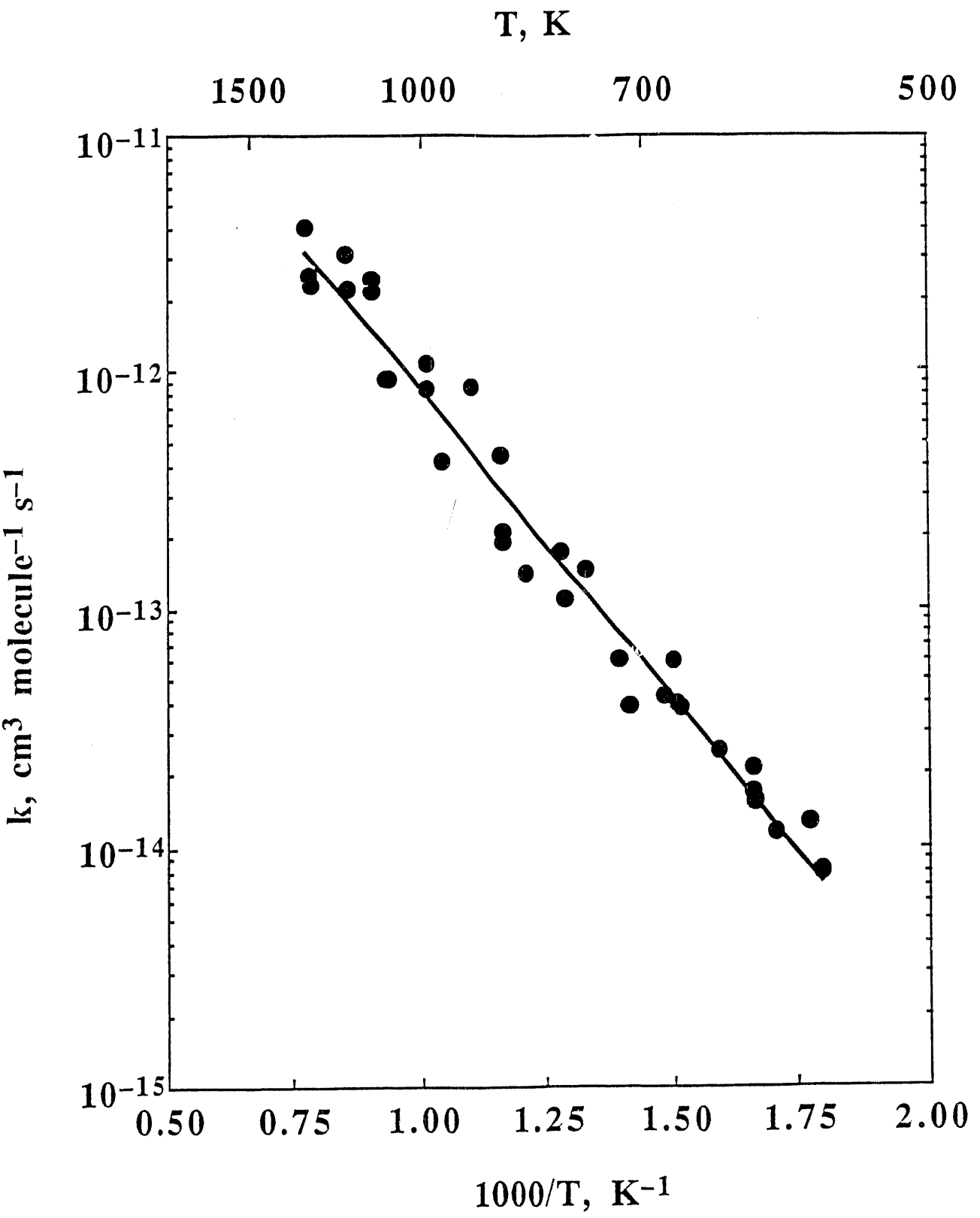
(●) present HTP study,

(▲) present LP–ST study,

(□) Wilson and O'Donovan,

(○) Westenberg and deHaas,

(———) best-fit to the combined HTP and LP–ST data, eq.(III).


T, K
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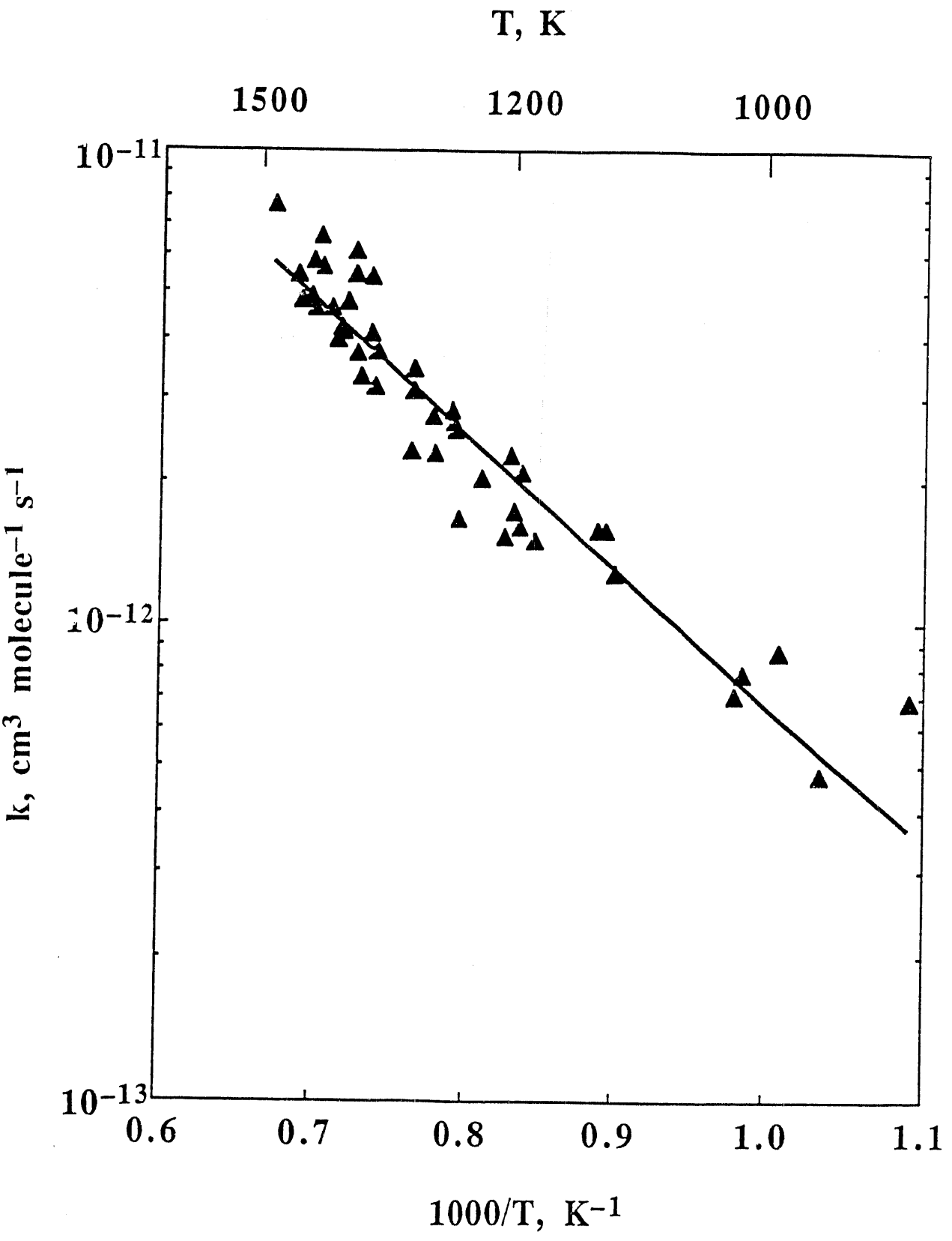
1000
700
500
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
k, cm^3 $molecule^{-1}$ s^{-1}
0.50
0.75
1.00
1.25
1.50
1.75
2.00
1000/T, K^{-1}

Figure 1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1000
10^{-11}
10^{-12}
10^{-13}
k, cm^3 $molecule^{-1}$ s^{-1}
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0.7
0.8
0.9
1.0
1.1
1000/T, K^{-1}

Figure 2

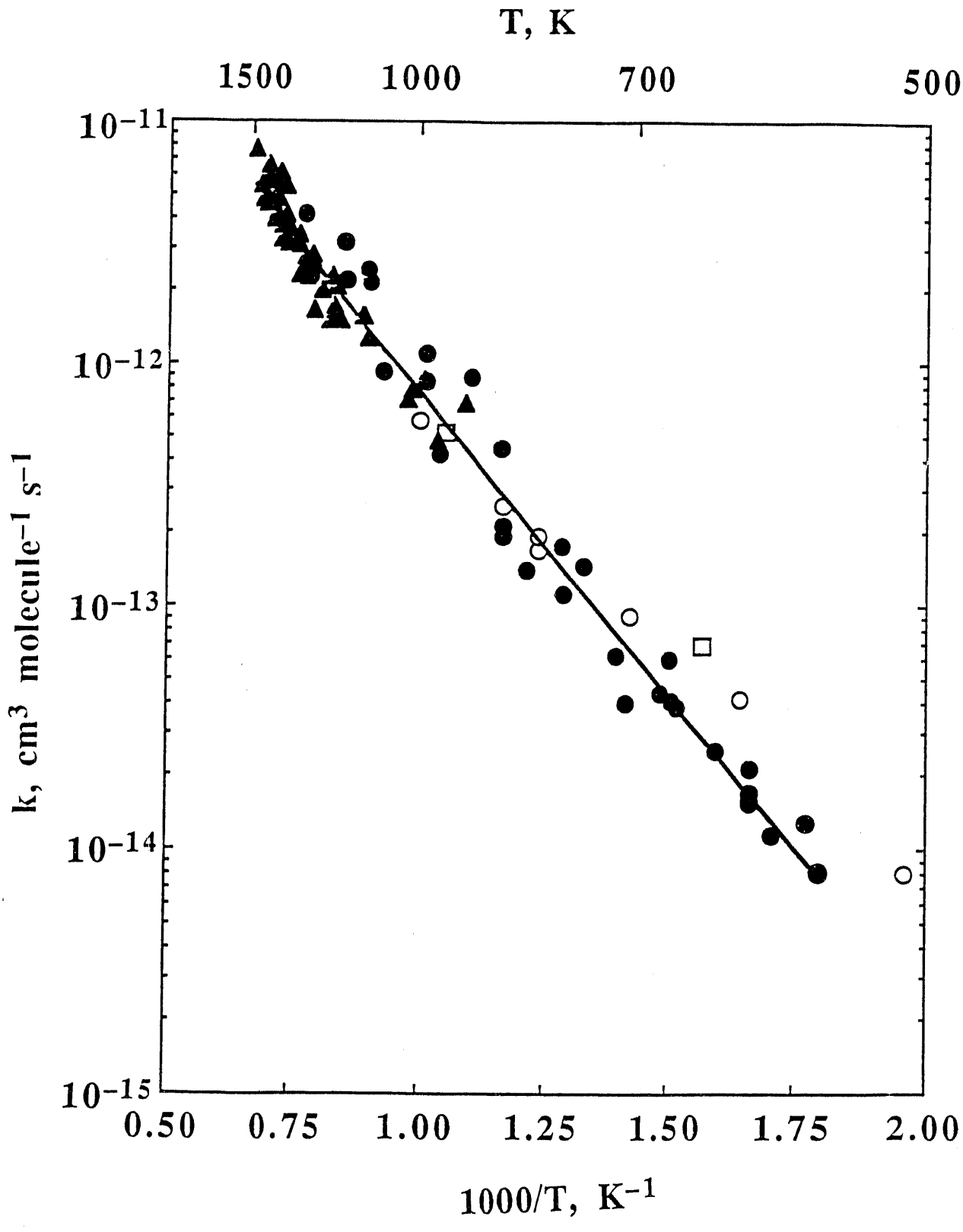
T, K
1500
1000
700
500
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
k, cm^3 $molecule^{-1}$ s^{-1}
0.50
0.75
1.00
1.25
1.50
1.75
2.00
1000/T, K^{-1}

Figure 3

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