THE RECOMBINATION OF METHYL RADICALS IN THE LOW PRESSURE LIMIT

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The rate constants for the recombination of methyl radicals in the low pressure limit are calculated between 300 and 1400 K, as well as the isotope effect for perdeutero substitution. The calculated low pressure rate constants are substantiated by data extrapolated from experiments in the fall-off range.

1. Introduction

The recombination of methyl radicals is one of the model reactions in gas kinetics. It has been extensively studied, and the literature up to 1971 has been summarized in ref. [1]. Since then the limiting high pressure rate constants have been remeasured and now appear to be well established over a wide range of temperatures [2,3]. For the fall-off range discrepancies of about two orders of magnitude still exist [1]. To obtain more accurate data in the fall-off range, the rate constants in the high pressure limit may be combined with calculated rate constants in the low pressure limit, using an established interpolation procedure [4]. Furthermore comparison of accurate calculated strong collision rate constants in the low pressure limit can yield essential information on the energy transfer properties of excited polyatomic molecules [5–7].

In the present work the rate constants for the recombination of methyl radicals are calculated in the low pressure limit between 300 and 1400 K, using a recent theoretical model [5–8]. The calculations are supported by the extrapolation of experimental data obtained in the fall-off range. The isotope effect for the perdeutero substitution is also calculated.

2. Calculation of the low pressure rate constants

It has been shown that rate constants for thermal dissociation and recombination reactions in the low pressure limit may be calculated with good accuracy over a wide temperature range using a new model in which rotational motion is treated rigorously [5]. In this model the strong collision rate constant is given by

$$k_{0,rec}^{sc} = \frac{[M] \, Z_{LJ} \, Q_{el} Q_t N}{Q_1 Q_2} \exp\left(E_0/kT\right)$$

$$\times \sum_{J=0}^{\infty} (2J+1) \int_{E_0(J)}^{\infty} \rho(E,J) \exp\left(-E/kT\right) dE. \quad (1)$$

Z_{LJ} is the Lennard-Jones collision frequency, Q_{el} is the electronic partition function of the molecule, Q_t is the translational partition function of the molecule per unit volume, N is Avogadro's number, and Q_1 and Q_2 are the molecular partition functions of the fragments per unit volume. $E_0(J)$ is the maximum of the lowest adiabatic channel for total angular momentum J [8]. For a symmetric top

$$\rho(E,J) \approx \sum_{K=0}^{J} g(K) \rho_{vib,h}(E_{vib}) F_{anh}(E_{vib}), \quad (2)$$

with $g(K) = 1$ if $K = 0$, and $g(K) = 2$ if $K \neq 0$, and $E_{vib} = E - BJ(J+1) - (A-B)K^2$. $\rho_{vib}(E_{vib})$ and $F_{anh}(E_{vib})$ were calculated from Haarhoff's expression for the harmonic density of vibrational states and the expression for the anharmonicity correction [9]. The rotational barriers $E_0(J)$ were calculated using van der Waals, Morse and Lennard-Jones (6,12) potential models for the reaction coordinate [5]. The van der Waals constant was estimated from the relation of

Slater and Kirkwood [10]. For the recombination of CH_3 or CD_3 radicals the effect of the different potential models on the calculated rate constants was shown to be small ($< 20\%$) between 300 and 1400 K.

To compare the calculated strong collision rate constants with the measured rate constants, a collision efficiency β_c ($\beta_c \equiv k_0/k_0^{sc}$) was calculated. Following refs. [6,7] we use $\beta_c = \beta_{\sigma\sigma} \beta_{c\Delta E}$ with $\beta_{\sigma\sigma} \approx 1$ and $\beta_{c\Delta E}$ defined by the relation

$$\beta_{c\Delta E}/[1-(\beta_{c\Delta E})^{1/2}] = - \langle\Delta E\rangle/F_E kT, \qquad (3)$$

where $\langle\Delta E\rangle$ is the average energy transferred per collision, which was taken to be independent of the temperature over the temperature range considered [6,11]. $\langle\Delta E\rangle$ was taken to be about $-110 \, cm^{-1}/mol$ for excited ethane molecules in collision with He, and about $-230 \, cm^{-1}/mol$ with Ar. These values of $\langle\Delta E\rangle$ were obtained by comparison of theory and experiment in refs. [6,7,11]. It was assumed that these values for $\langle\Delta E\rangle$ are the same for C_2H_6 and C_2D_6 [12]. F_E gives the energy dependence of the density of states which is defined as

$$F_E = \frac{\Sigma_{J=0}^{\infty} (2J+1) \int_{E_0(J)}^{\infty} \rho(E,J) \, e^{-E/kT} \, dE}{kT \, \Sigma_{J=0}^{\infty} (2J+1) \, \rho(E_0(J),J) \, e^{-E_0(J)/kT}}. \qquad (4)$$

The rate constants calculated for the reactions $CH_3 + CH_3 + M \rightarrow C_2H_6 + M$ and $CD_3 + CD_3 + M \rightarrow C_2D_6 + M$ (M = He or Ar) in the low pressure limit are listed in table 1. The values in parentheses are for M = Ar. The tabulated values were calculated with a Morse potential in which the zero-point energy was interpolated

Table 1

Rate constants. $k_{0,rec}$ (M)/[M] (10^{19} cm^6 mol^{-2} s^{-1}), for the thermal recombination of methyl and perdeutero methyl radicals in the low pressure limit for $300 \, K \leqslant T \leqslant 1400 \, K$ in He or Ar. The values for Ar are listed in parentheses. The values of β_c are calculated from eq. (3)

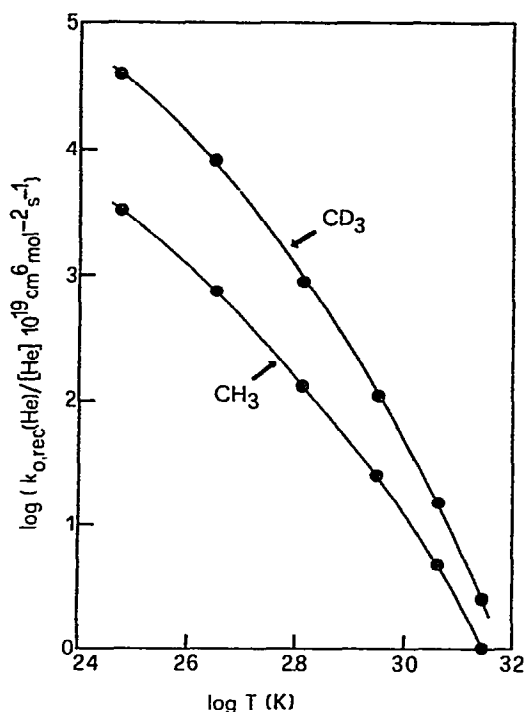| T (K)	$2CH_3 \xrightarrow{M} C_2H_6$	β_c	$2CD_3 \xrightarrow{M} C_2D_6$	β_c
300	3430	0.25	28600	0.25
450	745	0.18	4960	0.18
650	133	0.13	760	0.13
900	23	0.094	95	0.092
1150	4.8	0.071	15	0.069
1400	1.0	0.055	2.6	0.053
1400	(1.6)	(0.12)	(3.9)	(0.11)

Fig. 1. Calculated low pressure limiting rate constants for the thermal recombination of methyl or perdeutero methyl radicals in He between 300 and 1400 K.

exponentially between reactants and products using a second potential parameter α [5,8]. α for C_2H_6 and C_2D_6 was taken to be $1 \, Å^{-1}$ [8]. The data listed in table 1 for M = He are plotted in fig. 1. The isotope effect for the perdeutero substitution on the calculated rate constants increases with decreasing temperature. The large differences between the recombination rate constants in the low pressure limit for CH_3 and CD_3 radicals are to a large extent due to the differences in the densities of states. For the deuterated molecule the frequencies of several vibrational modes are significantly lower than for normal ethane, and thus at a particular energy the density of states is higher.

3. Experimental low pressure rate constants

. Comparison of the calculated low pressure limiting rate constants with experiment was performed by the extrapolation of reliable data in the fall-off range to the low pressure limit. This was done for methyl recombination at 450 and 1350 K, and for perdeutero

methyl recombination at 1350 K, using the method described in ref. [4].

The experimental data in the fall-off range at 1350 K were obtained by decomposing azomethane in a shock wave and monitoring the consequent recombination of methyl radicals by their absorption in the $^2A_1'$ $\leftarrow$ $^2A_2''$ system around 216 nm [3]. The measured [Ar] dependent second order rate constants k_{rec} are shown in fig. 2a. Following the method of ref. [4] these data were extrapolated to obtain the limiting high and low pressure rate constants by the use of reduced Kassel integrals. From the molecular data of C_2H_6 [13] and the collision efficiency β_c one derives effective values for the Kassel parameters of $S_K = 8.9$ and $B_K = 18$ at 1350 K. The corresponding reduced Kassel curve was fitted to the experimental data giving the limiting low and high pressure rate constants $k_{0,rec}(Ar)/[Ar] = 1.2 \times 10^{19}$ cm^6 mol^{-2} s^{-1}, and $k_{\infty,rec} = 2 \times 10^{13}$ cm^3 mol^{-1} s^{-1}. The uncertainty in the extrapolation to the high pressure limit is about 50%. The extrapolated low pressure rate constant is uncertain to a factor of 4 due to the long extrapolation. Within this uncertainty the calculated value of 2.8×10^{19} cm^6 mol^{-2} s^{-1} (which is uncertain to about a factor of 2) and the extrapolated
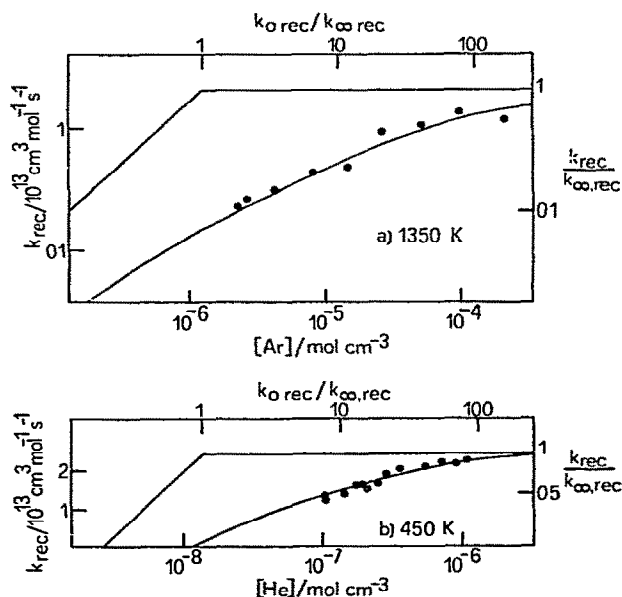

a) 1350 K

b) 450 K

Fig. 2. Fall-off curves for (a) the recombination of methyl radicals in Ar at 1350 K [3], and (b) the recombination of methyl radicals in He at 450 K [15]. ● are the experimental data.

measured value agree*. The fitted reduced Kassel curve is shown in fig. 2a together with the measured rate constants k_{rec} from ref. [3].

At 450 K the experimental data used for extrapolation from the fall-off range were obtained in the flash photolysis of dimethyl mercury diluted in He [15], where the concentration of methyl radicals was followed via the absorption at 216 nm [16]. The measured [He] dependent second order rate constants k_{rec} are shown in fig. 2b. The limiting high pressure rate constant $k_{\infty,rec} = 2.7 \times 10^{13}$ cm^3 mol^{-1} s^{-1} was measured directly in this case, rather than obtained by extrapolation. The uncertainty in this measurement is about 20%. For the extrapolation of the experimental data to the low pressure limit using reduced Kassel integrals, effective values for the Kassel parameters of $S_K = 4.3$ and $B_K = 22$ are derived. Fitting the corresponding reduced Kassel curve to the experimental data gives $k_{0,rec}(He)/[He] = 2.3 \times 10^{21}$ cm^6 mol^{-2} s^{-1}. The uncertainty in this extrapolation is about a factor of 4. Agreement of the calculated value $k_{0,rec}(He)/[He] = 7.4 \times 10^{21}$ cm^6 mol^{-2} s^{-1} and the extrapolated measured value is within this uncertainty. The measured rate constants k_{rec} together with the fitted reduced Kassel curve are shown in fig. 2b. Comparison of figs. 2a and 2b demonstrates that at 450 K the reduced fall-off curve is narrower than at 1350 K. $k_{\infty,rec}$ is nearly independent of temperature over a wide temperature range as predicted by the adiabatic channel model for unimolecular reactions [8], and at 1350 K the high pressure limit is reached for a much higher total pressure than at 450 K. $k_{0,rec}$ is shown to be strongly dependent on the temperature.

Our present analysis gives $P_{1/2}$ values for He at 450 K of 1.2×10^{-7} mol cm^{-3} (3.4 torr), and 7×10^{-5} mol cm^{-3} (5.9×10^3 torr) for Ar at 1350 K. These values should be compared with earlier data summarized in ref. [1], which at a given temperature show a scatter of about a factor of 100. It should be noted that the influence of the nature of the inert gas on $P_{1/2}$ cannot be neglected. To render the comparison of the present values for $P_{1/2}$ with the data of ref. [1] more satisfactory, we take C_2H_6 as a hypothetical collision partner, and correct for Z_{LJ}, β_c (taking $\langle \Delta E \rangle =$

-580 cm^{-1} [7]), and the shape of the reduced fall-off curve [4]. The values for $P_{1/2}$ (M = C_2H_6) estimated in this way are 1.1 torr and 1950 torr at the respective temperatures of 450 and 1350 K. Extrapolation of the data for recombination of perdeutero methyl radicals [3,14] to the low pressure limit yielded $k_{0,rec}(Ar)/$ [Ar] = 7×10^{19} cm^6 mol^{-2} s^{-1}. Within the uncertainty of this extrapolation of about a factor of 4 this value agrees with the calculated value of $k_{0,rec}(Ar)/$ [Ar] = 7.7×10^{19} cm^6 mol^{-2} s^{-1}.

With the available data on the low pressure limiting rate constants for methyl radical recombination over a wide temperature range the ethane/methyl radical system has become one of the particularly complete studies in gas kinetics.

Acknowledgement

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