Influence of Temperature on the Removal Rates of $CH_2(\tilde{a}\,^1A_1)$ by Inert Gases and Hydrocarbons

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The reactions of $CH_2(\tilde{a}\,^1A_1)$ with the inert gases He, Ar, N_2, with H_2 and with the hydrocarbon reactants CH_4, C_2H_6, C_2H_4 and C_6H_6 have been investigated at 210, 295 and 475 K. $CH_2(\tilde{a}\,^1A_1)$ was generated by pulsed laser photolysis in a quasistatic thermostated gas cell and detected by pulsed laser induced fluorescence. Concentration profiles of $CH_2(\tilde{a}\,^1A_1)$ were recorded under first order reaction conditions by varying the time delay between the photolysis and the probe laser pulses.

The second order rate constants determined at room temperature are in good agreement with those of earlier work. No differences between the removal rates of ortho-and para-methylene nuclear spin states by the inert gases were observed. The experimental rate constants were fitted to an expression $k = A \cdot (T/295\ \mathrm{K})^n$. The results are given in the form $\{A \pm \Delta A\}\ (n \pm \Delta n)$ with A in units of $10^{13}\ \mathrm{cm^3/mol \cdot s}$:

He: $\{0.15 \pm 0.03\}\ (+1.26 \pm 0.1)$, Ar: $\{0.29 \pm 0.06\}\ (+0.75 \pm 0.25)$,
N_2: $\{0.42 \pm 0.08\}\ (+1.0 \pm 0.3)$, H_2: $\{7.3 \pm 1.0\}\ (-0.5 \pm 0.6)$,
CH_4: $\{4.3 \pm 0.5\}\ (-0.95 \pm 0.35)$, C_2H_6: $\{10 \pm 1.5\}\ (-0.90 \pm 0.15)$,
C_2H_4: $\{14 \pm 2\}\ (-0.82 \pm 0.15)$, C_6H_6: $\{24 \pm 4\}\ (-0.55 \pm 0.35)$.

1. Introduction

The reactions of singlet methylene $CH_2(\tilde{a}\,^1A_1)$ (abbreviated as $^1CH_2$ throughout this paper) have been investigated directly in some detail during recent years after lasers became available as powerful tools for its generation and detection [1–7]. Kinetic experiments have been carried out at room temperature for a number of reactants including inert gas quenchers, saturated and unsaturated hydrocarbons as well as inorganic substances. It has been established that $^1CH_2$ reacts very fast with nearly all reactants investigated. Its slowest reaction was found to be collision induced "intersystem crossing" (ISC) by Helium with a rate constant of $2 \cdot 10^{12}\ \mathrm{cm^3/mol\,s}$ at room temperature [1, 2]. The reaction rates were determined to be very close to the gas kinetic collision number for those molecules, whose primary addition or insertion products can undergo exothermic unimolecular dissociation reactions or whose products can be collisionally stabilized [1–7].

Also the kinetics of ground state methylene $CH_2(\tilde{X}\,^3B_1)$ (abbreviated as $^3CH_2$) with a number of organic compounds was explored using the discharge-flow technique in connection with far infrared laser-magnetic resonance (LMR) absorption for the detection of $^3CH_2$ [8–14]. These experiments were carried out in the range 295–700 K. For hydrocarbon reactants, the room temperature rate constants of the $^3CH_2$ reactions were determined to be five or six orders of magnitude smaller than those for $^1CH_2$. The $^3CH_2$ rates exhibit considerable activation energies. Since the singlet-triplet energy gap $\Delta E_{\mathrm{S\text{-}T}}$, measured in LMR experiments with spectroscopic accuracy [15, 16], is only 37.8 kJ/mol, it turned out that the reactions of methylene in its two lowest electronic states cannot be treated separately. The mutual interconversion of $^1CH_2$ and $^3CH_2$ in collisions with bath gas molecules has to be taken into account especially at higher temperatures for a proper description of thermal methylene reaction systems, for example in combustion processes. This has been done in the work on $^3CH_2$ reactions cited above with the assumption that the rates of the $^1CH_2$ reactions did not depend on temperature. Of course no strong temperature dependence can reasonably be expected, because the rates are mostly near the gas kinetic collision number at room temperature. Nevertheless, details of methylene reactions with both spin states participating depend on whether the reaction rates of $^1CH_2$ are weak positive or negative functions of temperature. Moreover,

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recent theoretical work on the mechanism of the collision induced "intersystem crossing" (ISC) of $^1CH_2$ by inert gas quenchers indicated some positive temperature dependence for these rate coefficients [17, 18].

In this study the reaction rates of $^1CH_2$ with the inert gases He, Ar and N_2, with H_2 and with the prototypical hydrocarbons CH_4, C_2H_6, C_2H_4 and C_6H_6 are investigated in the range 210–475 K using the pulsed laser photolysis/laser induced fluorescence (LIF) technique for the generation and detection of $^1CH_2$.

2. Experimental

The experimental set-up has been described in earlier communications [19–22]. $^1CH_2$ is generated by pulsed laser photolysis of CH_2CO and detected by pulsed LIF with the photolysis and probe laser beams counterpropagating through a quasistatic vacuum gas cell. The apparatus is equipped with a gas supply system (Tylan FC 280, RO 701 FC) providing a slow constant gas flow of a mixture of He, CH_2CO and the reactant R to avoid accumulation of reaction products between two laser shots. The pressure in the gas cell, typically 1 mbar, is measured with capacitance manometers (MKS Baratron 220). Hollow cylinders, mounted inside the gas cell, are used to thermostate the gas mixtures when they flow along the inner walls of the insets. The detection volume is completely encircled by the cylinders, except for appropriate holes in the directions of the laser beams and fluorescence detection. Temperatures up to 550 K are reached by electrical heating with a heating coil in the wall of the cylindrical inset. The temperature is measured by a Pt-100 resistance thermometer and regulated to within ± 2 K with an electronic control unit.

A refrigerant, flowing from a cryostat through the low temperature inset, cools the gas cell down to 205 K at minimum. The temperature inside is determined by measuring the temperature of the cooling agent at the inlet and the outlet of the inset. These values are found to differ by a few K only, and a mean value is adopted. Experiments both at higher and lower temperatures with a calibrated thermocouple showed that the temperature of the gas phase coincides within ± 5 K with the wall temperatures determined in this manner.

The photolysis pulses are provided by an excimer laser (Lambda Physik EMG 101) operating on the XeCl line at $\lambda = 308$ nm. At this wavelength, the photolysis of CH_2CO is known to produce $CH_2(\tilde{a}\,^1A_1)$ with a quantum yield near unity [23–25]. After a variable time delay, the excimer pumped dye laser (Lambda Physik LPX 205, FL 3002) excites an appropriate rotational line in the vibronic transition $CH_2(\tilde{b}\,^1B_1\ 0,14,0 \leftarrow \tilde{a}\,^1A_1\ 0,0,0)$. In the experiments with the hydrocarbons this is generally the very strong line $J = 4$ in the $^PQ_{1,J}$-branch near $\lambda = 590.71$ nm. One of the purposes of this study was to investigate whether the physical quenching rates for the ortho nuclear spin states with $K_a + K_c = 2n + 1$ (odd $K_a + K_c$) and the para nuclear spin states with $K_a + K_c = 2n$ (even $K_a + K_c$) of $^1CH_2$ show any systematic difference. Therefore this Q-branch transition is not very well suited for the experiments with the inert gases because its line spacing is not much larger than the bandwidth of the exciting dye laser ($\Delta\tilde{\nu} = 0.2\ \mathrm{cm}^{-1}$). Hence the lines $J = 2$ and $J = 3$ of the $^PR_{1,J-1}$ branch, where the line spacing is more than one order of magnitude larger than the dye laser linewidth, are chosen at $\lambda(J=2) = 589.51$ nm and $\lambda(J=3) = 589.37$ nm [26, 27].

The LIF signals are observed at right angles with respect to the laser beam axis through a cut-off filter (Schott RG 630) with a photomultiplier (EMI 9817 QB). They are stored and averaged over 32–64 pulses by a transient digitizer (Tektronix 7912 AD) and then integrated and processed further with a mini-computer (PDP 11/34).

Chemicals with the highest commercial available purity are used throughout without further purification. CH_2CO is prepared by pyrolysis of $(CH_3)_2CO$ at 1000 K and condensed at 195 K. It is distilled several times under vacuum from trap to trap to obtain a purity of >99%. It is stored in the dark at 77 K and dosed into the cell from an evacuated, dry-ice cooled bulb during the experiments. C_6H_6 is evaporated in a two stage thermostated saturator with He as carrier gas.

3. Results

The composition of the gas mixture is chosen such that removal of $^1CH_2$ in collisions can be described by a first order rate law. Typically the mixture consists of 1 mbar He as a bath gas, 0.002 to 0.006 mbar CH_2CO and, depending on its reactivity, a variable partial pressure of the reactant in the range 0.005–5 mbar.

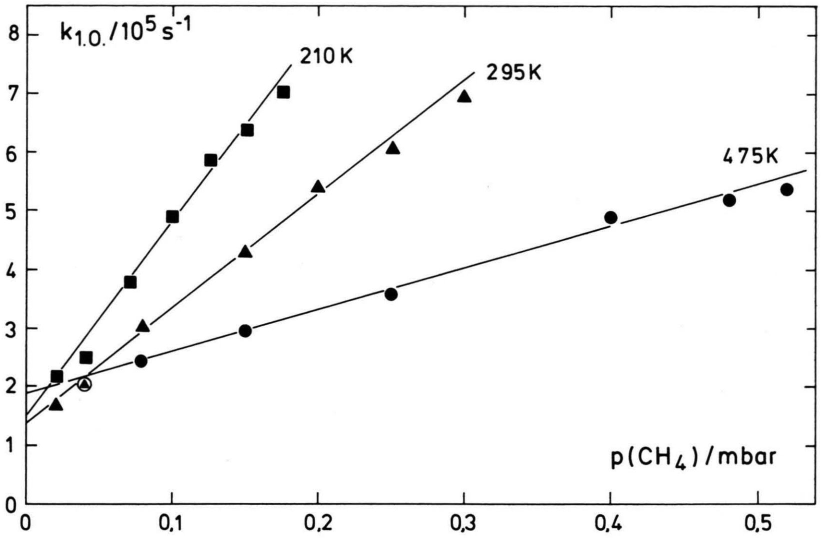

Fig. 1. First order rate constants as functions of reactant pressure for the reaction of ${}^1CH_2$ with CH_4.

Hence, the reaction scheme consists of the formation of ${}^1CH_2$ by photolysis,

$$CH_2CO + h\nu(\lambda = 308\text{ nm}) \rightarrow CH_2(\tilde{a}\,{}^1A_1) + CO, \quad (1)$$

and the subsequent collisional removal processes of ${}^1CH_2$:

$$\begin{aligned} {}^1CH_2 + R &\rightarrow \text{products}, && (2)\\ &\rightarrow {}^3CH_2 + R, && (2a)\\ &\rightarrow \text{chemical products}, && (2b)\end{aligned}$$

$$\begin{aligned} &{}^1CH_2 + He \rightarrow {}^3CH_2 + He, && (3)\\ &k_3 = 2 \cdot 10^{12}\text{ cm}^3/\text{mol s } [1, 2] \end{aligned}$$

$$\begin{aligned} &{}^1CH_2 + CH_2CO \rightarrow \text{products}, && (4)\\ &k_4 = 1.6 \cdot 10^{14}\text{ cm}^3/\text{mol s } [2, 21]. \end{aligned}$$

Since only several tenth of a percent of the CH_2CO are photolyzed by a single photolysis laser pulse, the concentration of each of the collision partners of ${}^1CH_2$ is at least two orders of magnitude higher than the concentration of ${}^1CH_2$. Consecutive reactions can thus be omitted from the kinetic scheme. The concentration profile of ${}^1CH_2$ is directly monitored by observation of the LIF intensity I_F as a function of the delay time Δt between the photolysis and the probe laser pulses. According to a first order rate law, plots of $\ln I_F$ versus Δt in the range $3\,\mu s \leqq \Delta t \leqq 8\,\mu s$ yield straight lines for all reactants with rate constants

$$k_{1.o.} = k_2(R)\,[R] + k_3[He] + k_4[CH_2CO]\,.$$

Helium is not added to the reactants Ar and N_2, i.e. then $k_3[He] = 0$. No signals for $\Delta t \leqq 3\,\mu s$ are included in the data analysis because ${}^1CH_2$ is generated rotationally hot in the photolysis [2, 27] and the low rotational states are being collisionally populated during this period. For the highest reactant pressures applied the signal/noise ratio becomes too low at $\Delta t > 8\,\mu s$ and thus no signals of this time range are analyzed.

The $k_{1.o.}$ are plotted against the reactant pressures and show good linear correlation for all substances. The second order rate constants are evaluated by linear regression. Figure 1 shows plots of this kind for $R = CH_4$ at 210, 295 and 475 K. The measurements were carried out at these three temperatures for all reactants, except for C_6H_6. In this case the lowest temperature was 218 K in order to ensure that the maximum partial pressure of C_6H_6 is low compared to its vapor pressure. The non-zero intercepts of the graphs in Fig. 1 result from reaction of ${}^1CH_2$ with He and CH_2CO.

The experimental results for the physical deactivation of ${}^1CH_2$ by He, Ar and N_2 at 475 K are shown in Figure 2. The filled symbols correspond to profiles taken for the ${}^1CH_2$ rotational level $J_{K_a K_c} = 3_{12}$, while the unfilled symbols refer to the $J_{K_a K_c} = 2_{11}$ state. Within the error limits no systematic difference between the removal rates of these two rovibronic levels of ${}^1CH_2$ is found at this nor at the lower temperatures. Hence, the values for the second order rate constants

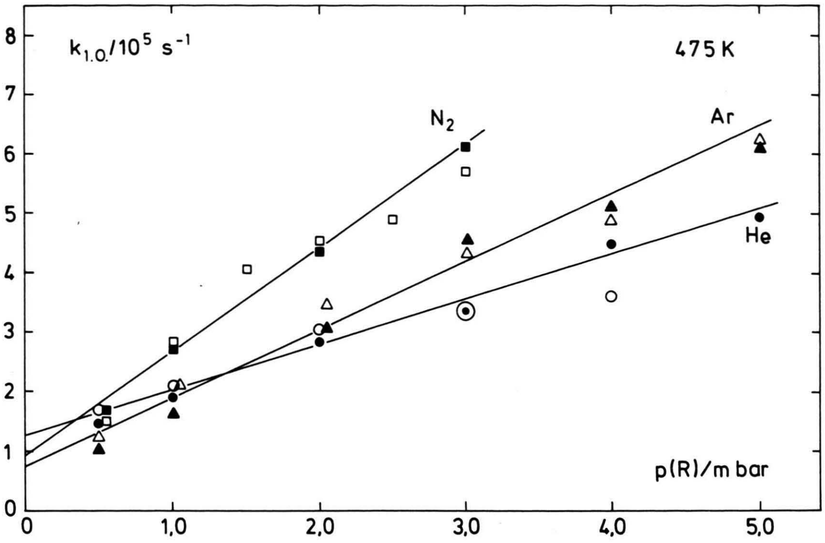

Fig. 2. First order rate constants as function of reactant pressures for the reaction of $^1CH_2$ with He, Ar, and N_2 at 475 K. The filled symbols correspond to experiments where the $J_{K_aK_c} = 3_{12}$ level was probed, while the open symbols refer to concentration vs. time profiles of the $J_{K_aK_c} = 2_{11}$ state.

Table 1. Second order rate constands k_2(R) and the A-factors are given in units of 10^{13} cm^3/mol s. The error limits correspond to 2σ plus estimated calibration errors. The values in the last two columns were obtained by fitting the rate coefficients to an expression $k = A\,(T/295\ K)^n$ as described in the text.

R	k_2(R)			A	n
	210 K	295 K	475 K		
He	0.10 ± 0.02	0.15 ± 0.03	0.28 ± 0.05	0.15 ± 0.03	1.26 ± 0.1
Ar	0.23 ± 0.04	0.28 ± 0.06	0.42 ± 0.07	0.29 ± 0.06	0.75 ± 0.25
N_2	0.29 ± 0.04	0.44 ± 0.08	0.65 ± 0.08	0.42 ± 0.08	1.0 ± 0.3
H_2	8.4 ± 1.0	8.1 ± 1.0	5.6 ± 0.6	7.3 ± 1.0	-0.5 ± 0.6
CH_4	5.8 ± 0.8	4.6 ± 0.5	2.7 ± 0.5	4.3 ± 0.5	-0.95 ± 0.35
C_2H_6	14 ± 1	10 ± 1.5	6.7 ± 1.0	10 ± 1.5	-0.90 ± 0.15
C_2H_4	19 ± 3	15 ± 2	9.7 ± 1.5	14 ± 2	-0.82 ± 0.20
C_6H_6	31 ± 4 *	24 ± 4	20 ± 4	25 ± 4	-0.55 ± 0.35

* $T = 218$ K.

given below are derived from linear regressions including both these nuclear spin states.

The rate constants determined in this manner are collected in Table 1. The errors given for the second order rate coefficients correspond to twice the standard deviation of the slopes of the $k_{1.O.}$ vs. p(R) plots plus estimated uncertainties in the pressure and flow calibrations. The rates are fitted to an expression

$$k_2(\mathrm{R}) = A \cdot \left(\frac{T}{295\ \mathrm{K}}\right)^n$$

via a linear regression of $\log k_2(\mathrm{R})$ as a function of $\log T$. The A-factor thus corresponds to the reaction rate at 295 K. For most of the reactants these fits correlate slightly better than the Arrhenius plots (ln k versus $1/T$), but this is hardly significant. The Arrhenius expressions for the hydrocarbons are given in the discussion for comparison with the corresponding terms for the reactions of $NH(a\,^1\Delta)$, $O(^1D_2)$ and $CH(X\,^2\Pi)$. The factors A and the exponents n are given in the last two columns of Table 1. Three times the standard deviation is given for the error of n. The error limits for the A-factors correspond o the experimental errors in the determination of k_2(R) at 295 K.

4. Discussion

For the removal of $^1CH_2$ by the reactants investigated in this study room temperature rate constants have been determined in earlier investigations of this and other groups. The data are in good agreement with the rates for 295 K displayed in Table 1. For the inert gases the rates of Ashfold et al. [1] and of Langford et al. [2] seem to be systematically slightly higher than those evaluated here. However, the discrepancies do not exceed 30%. This is probably due to the fact that no corrections for diffusive loss of $^1CH_2$ were applied to the rates determined in this study. For H_2 and the aliphatic hydrocarbons the rate coefficients of [1, 2] are practically identical to those of this study. The reaction of $^1CH_2$ with C_2H_4 is found somewhat faster here than in [2], a problem which has already been discussed before [5]. The rate constant for R = C_6H_6, which had been determined in earlier, independent work [3], could be reproduced exactly.

From Table 1 it becomes clear that the temperature dependence of the rate of ISC in collisions of $^1CH_2$ with He, Ar, and N_2 is distinctively different from that of the predominantly chemically reactive removal with hydrocarbons. For the physical quenching with the inert gases a positive temperature exponent of $n = 1.0 \pm 0.25$ is determined. This is not unexpected, although in the earliest direct experimental investigation of this problem using LIF detection of $^1CH_2$ it was concluded that collision induced ISC of $^1CH_2$ is dominated by long range attractive forces [1], which usually implies a weak negative temperature dependence ($-1 \leqq n \leqq 0$). This conclusion was drawn, because a Parmenter-Seaver type correlation [29, 30] emerged between the cross sections $\sigma(R)$ and the intermolecular well depths $\varepsilon(CH_2{-}R)$ for R = He, Ne, Ar, N_2, Kr and Xe.

More recently, collision induced ISC of $^1CH_2$ has been described on a state resolved level of detail without adjustable parameters [17]. The physical quenching rates of $^1CH_2$ by He, Ar and N_2 and by CH_4 at room temperature have been computed semi-empirically. The calculations connected experimental results of LMR-spectroscopy [15, 17, 31], LIF, and magnetic rotation spectroscopy [27, 28] with the mixed electronic state model proposed by Gelbart and Freed [32, 33]. Following Bley et al. [17], intersystem crossing of $^1CH_2$ is mediated by a few discrete, strongly perturbed rovibrational levels of $^1CH_2$, which have to be described as being of mixed electronic parentage. These states are collisionally stabilized in the triplet manifold via a mechanism which resembles intensity borrowing in spectroscopy (for more details see [17, 31–33]). The results are in good agreement with experimental values [17, 31].

The temperature dependence of the quenching rates should be governed by the Boltzmann population of the discrete, well known strong coupling levels of $^1CH_2$ as a function of temperature. This results in a pronounced positive temperature dependence, which would overcompensate the weak negative function of temperature resulting from long range attractive intermolecular forces. Preliminary calculations yield a value of $n \approx 1$ at $T \leqq 600$ K [18]. This is in good agreement with the experimental results of this study.

For comparison: physical quenching rates of the isoelectronic $O(^1D_2)$ increase distinctly weaker or even decrease with temperature ($-1.0 \leqq n(^1O) \leqq +0.4$) [34, 35]. Corresponding investigations of the quenching of $NH(a\,^1\Delta)$ are currently in progress [36]. The results of this study lend further support to the ISC-mechanism for $^1CH_2$ developed in [17].

Systematic differences in the removal rate of ortho- and para-nuclear spin state levels of $^1CH_2$ were considered to be possible [17, 37], because the methylene nuclear spin angular momentum is conserved on the time scale of interest here and because there are differences in the number as well as in the degeneration and Boltzmann weighting factors of the strongly coupled levels of ortho- and para-symmetry, respectively. However, pronounced systematic discrepancies in the removal rates of the 2_{11}- and the 3_{12}-level studied here are found neither in the absolute values nor in the temperature dependence. This agrees with the result reported in [2] that removal of the $^1CH_2$ rotational levels 1_{10}, 3_{13}, 4_{14} and 7_{16} by N_2 proceeds with identical rate at room temperature.

In contrast to the purely physical quenchers, the reactions of $^1CH_2$ with hydrocarbons, where exothermic chemical paths dominate, become slower with increasing temperature. The values of the exponent n determined for H_2 and the aliphatics CH_4 and C_2H_6, for the olefin C_2H_4 and for the aromatic C_6H_6 do not differ markedly. This similarity, and the fact that the room temperature removal rates of $^1CH_2$ by the higher alkanes C_3H_8 and C_4H_{10}, by olefinic, acetylenic and aromatic hydrocarbons [2, 3, 5, 7] are nearly equal, suggest that the rates for the reactions of $^1CH_2$ with hydrocarbons in the gas phase become generally smaller at higher temperature. Preliminary experiments indicate that this is true also for those inorganic compounds which also react very fast with $^1CH_2$ at room temperature, e.g. NH_3 [6]. This is consistent with the mechanistic picture of $^1CH_2$ being captured in an effective "potential energy trap" without activation barrier in the reaction coordinate, which was assumed in the data analysis of the $^3CH_2$ rate measurements in [9–12]. A quantitative reevaluation will reveal some corrections of the temperature dependent branching ratio of direct triplet reaction versus activation to $^1CH_2$ in those cases, where the experimental activation energy is close to the singlet-triplet energy gap. More details will be published [13, 14].

One may speculate about the consequences of the results reported here for reactions of CH_2 at higher temperatures. For the noble gases, the results show that the rate of collision induced ISC increases with increasing temperature. According to the mixed state model, the mechanism of the ISC should not depend too strongly on the individual properties of the colliders. The reason for this is that the decisive factor for ISC in CH_2 is the strong coupling between discrete singlet- and triplet-levels, which is a purely intramolecular effect. The task of the collision partner is the rotational relaxation of the "doorway states" into the triplet manifold [17]. Thus it seems to be a reasonable assumption that the temperature behaviour of the rates of the collision induced ISC channels is similar for inert gas quenchers and for reactants with competing chemical channels. This would mean that in the reaction of $^1CH_2$ with a hydrocarbon the rate constant for ISC $k_{2a}(R) \sim T^{n_a}$ should have a positive n_a within the range $0 \leqq n_a \leqq 1$.

On the other hand, the overall removal rate constants $k_2(R)$ for the hydrocarbons, which include both the rates of ISC and chemical reaction pathways, become smaller at higher temperatures. The rates of chemical reactions thus have to decrease with increasing temperature. In fact, the chemical reaction rates are likely to decrease even stronger with temperature than the overall removal rates. The temperature dependences of the overall removal rates thus would result from a partial compensation of the two contrary temperature functions. Hence the contribution, relative and absolute, of ISC to the total consumption of $^1CH_2$, $k_{2a}(R)/k_2(R)$, may increase with temperature over a limited temperature range.

For a more detailed discussion, the rate expression $k_2(R) = k_{2a}(R) + k_{2b}(R)$ with independent contributions of ISC and chemical reaction of $^1CH_2$ shall be used. This is suggested by isotopic exchange experiments in the system $^1CH_2{-}CD_4/^1CD_2{-}CH_4$ [31]. For an arbitrary hydrocarbon it shows the following temperature dependence in the T-range covered here:

$$k_2(R) = A \cdot (T/295\text{ K})^n$$

with $-1.0 \leqq n \leqq -0.5$, similar to the expressions determined in this work. The branching ratio of ISC over total removal may be $k_{2a}(R)/k_2(R) = 0.25$ at room temperature, as suggested by investigations with a great number of hydrocarbons [3, 5, 8]. The rate of ISC shall vary with temperature as for inert collision partners

$$k_{2a}(R) = (0.25\text{ A})(T/295\text{ K})^{n_a}.$$

Let us assume for simplicity that the rate of the chemical reaction varies with temperature in a similar way like

$$k_{2b}(R) = (0.75\text{ A})(T/295\text{ K})^{n_b}.$$

As mentioned above, collision induced ISC and complex formation via insertion of $^1CH_2$ (or $^1CD_2$) into C−H bonds seem to be independent elementary reactions. Therefore the temperature dependence of their rate constants may be given by two independent expressions.

The rate constant $k_{2b}(R)$ can then be calculated for any given temperature via $k_{2b}(R) = k_2(R) - k_{2a}(R)$, if a reasonable power law for $k_{2a}(R)$ is assumed. The exponent n_b may be obtained from a fit of $\log(k_{2b}(R))$ vs. $\log T$. Obviously n_b is a function of n and n_a. It turns out that $-2.0 \leqq n_b \leqq -1.0$ in the temperature range covered by the experiments (210−475 K), if the input parameters n and n_a are varied between $-1.0 \leqq n \leqq -0.5$ and $0.5 \leqq n_a \leqq 1.0$. These values of n_b are reasonable for bimolecular "recombination" reactions without energy barrier.

Table 2 gives a survey of the influence of n_a and n_b on the contribution of ISC to the total removal rate of $^1CH_2$, $k_{2a}(R)/(k_{2a}(R) + k_{2b}(R))$, within the tempera-

Table 2. The contribution of ISC to the total removal of $^1CH_2$, $k_{2a}(R)/(k_{2a}(R) + k_{2b}(R))$, by an arbitrary hydrocarbon is given as function of temperature. Independent power laws are assumed for the temperature dependence of $k_{2a}(R)$ and $k_{2b}(R)$ as described in the text. The input parameters n_a and n_b are given in the first column.

$T/295$ K	0.75	1.0	1.5	2.0	3.0	4.0	5.0	7.0
T/K	221	295	443	590	885	1180	1475	2065
$n_a = +0.5$ $n_b = -1.0$	0.18	0.25	0.38	0.48	0.63	0.72	0.79	0.86
$n_a = +0.5$ $n_b = -2.0$	0.14	0.25	0.46	0.65	0.84	0.91	0.95	0.97
$n_a = +1.0$ $n_b = -1.0$	0.16	0.25	0.43	0.57	0.75	0.84	0.89	0.94
$n_a = +1.0$ $n_b = -2.0$	0.13	0.25	0.53	0.72	0.90	0.95	0.98	0.99

ture range of the experiments and extrapolated to $T/295\text{ K} \leqq 7$. n_a and n_b are chosen as parameters within the limits given above.

It emerges that $k_{2a}(R)/k_2(R)$ takes values close to $k_{2a}(R)/k_2(R) = 1$, if n_a is kept constant $n_a = 1.0$ up to $T \geqq 1000$ K. This is not very probable for $T > 1000$ K. Assuming the somewhat weaker temperature dependence $k_{2a}(R) \sim T^{0.5}$ yields lower branching ratios in the high temperature range of interest for flame and combustion chemistry [38–40]. The total removal rate constant of $^1CH_2$, $k_2(R)$, shows a shallow minimum below 1000 K and increases towards higher temperatures because of the increasing $k_{2a}(R)$. However, $k_{2a}(R)/k_2(R)$ invariably converges to the upper limit of 1 at very high temperatures. There is a possibility, depending on the population (and number) of the close coupling states, that the specific effects observed at moderate temperatures in this work do level off towards higher temperatures. Hence, $k_{2a}(R)/k_2(R)$ may increase steadily with increasing temperature up to about 1000 K (perhaps to a value around $k_{2a}(R)/k_2(R) \cong 0.6$) and then become practically independent of T.

As a consequence, the interconversion of the two methylene spin states by collisional activation of $^3CH_2$ and deactivation of $^1CH_2$ would be considerably accelerated towards higher temperatures. This does, however, not mean a higher net conversion rate of CH_2 in thermal reaction systems, because the irreversible chemical consumption of $^1CH_2$ slows down. Actually this is the reason why the conclusions of [9–12] concerning the rates of $^3CH_2$ reactions remain practically valid at high temperatures. However, in order to confirm these conjectures quantitatively, an experimental determination of $k_{2a}(R)/k_2(R)$ as function of temperature is required at high temperatures.

5. Comparison with Similar Radicals

The results of this study may be compared with the corresponding results for $NH(a\,^1\Delta)$, for $O(^1D_2)$ and for $CH(X\,^2\Pi)$. The nitrene radical and the oxygen-atom in their triplet ground states ($NH(X\,^3\Sigma^-)$ and $O(^3P_2)$) and metastable lowest singlet states ($NH(a\,^1\Delta)$ and $O(^1D_2)$) are isoelectronic to $^3CH_2$ and $^1CH_2$, respectively. The rate constants determined at room temperature for $NH(a\,^1\Delta)$ reactions show good correlation with those of $CH_2(\tilde{a}\,^1A_1)$ for many reactants [22, 41]. The reactivity of $NH(a\,^1\Delta)$ is generally somewhat lower than that of $^1CH_2$. $O(^1D_2)$ reacts very fast in chemical channels, if clearly exothermic dissociation paths are open for a primary addition-/or insertion-product. CH is an interesting radical for combustion and flame chemistry. It is also an electron deficient, highly reactive radical with second order reaction rates near the gas kinetic collision number. From an orbital symmetry point of view its ground state $CH(X\,^2\Pi)$ is similar to $CH_2(\tilde{a}\,^1A_1)$, while its first excited quartet state $CH(a\,^4\Sigma^-)$ resembles $CH_2(\tilde{X}\,^3B_1)$ [42–44].

Table 3 shows the "Arrhenius activation energies" for the reactions of the radicals $CH_2(\tilde{a}\,^1A_1)$, $NH(a\,^1\Delta)$ [45], $O(^1D_2)$ [46], and $CH(X\,^2\Pi)$ [42] with H_2 and the hydrocarbon reactants. The experiments for $^1CH_2$ (210–475 K, this study), for ^1NH (250–600 K, [45]) and for ^2CH (250–670 K, [42]) were carried out within similar temperature domains. The error limits for the $^1CH_2$ reactions are 3σ of the $\ln k$ versus $1/T$ plots, because of the small number of points. Those for the ^1NH and ^2CH reactions are quoted by the authors of [42, 45] as 2σ. Rate constant measurements for chemical reactions of $O(^1D_2)$ were performed at 200–350 K. The second order rate coefficients for H_2 and CH_4, and also for NH_3, H_2O, and HCl were found to be independent of temperature in these experiments [35, 46].

This behaviour of $O(^1D_2)$ is somewhat intermediate between $^1CH_2$ and ^2CH on the one hand and ^1NH on the other hand. Since both ^2CH and $^1CH_2$ are strongly electrophilic, their reactions are dominated by purely attractive long range forces, and the cross sections for addition and insertion become smaller at higher temperatures. ^1NH reacts somewhat more selectively. Its reactions with H_2 and CH_4 are associated with a distinctively positive activation energy, possibly required for abstraction of an H-atom [45]. The

Table 3. "Arrhenius activation energies" in kJ/mol for the reactions of $^1CH_2$, ^1NH [45], $O(^1D_2)$ [46] and ^2CH [42] with H_2 and the hydrocarbons investigated in this study. The error limits are explained in the text.

R	$CH_2(\tilde{a}\,^1A_1)$	$NH(a\,^1\Delta)$	$O(^1D_2)$	$CH(X\,^2\Pi)$
H_2	-1 ± 2	$+6.4 \pm 0.4$	0	-4.3 ± 0.4*
CH_4	-2.4 ± 1.8	$+7.8 \pm 0.2$	0	-1.7 ± 0.3
C_2H_6	-2.3 ± 0.4	–	–	-1.1 ± 0.25
C_2H_4	-2.1 ± 1.2	-1.1 ± 0.8	–	-0.72 ± 0.15
C_6H_6	-1.5 ± 0.5	–	–	0

* The activation energy becomes positive at $T > 400$ K, because formation of $CH_2(\tilde{X}\,^3B_1)$ is exothermic then.

rate of the electrophilic addition to C_2H_4, however, decreases with increasing temperature. This is probably true also for the reaction of ^1NH with C_6H_6 [47] and for the reactions of $O(^1D_2)$ with π-bonding systems [48], for which the room temperature rate constants are found to be very high.

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