

RATE CONSTANTS FOR CH(X²Π) REACTIONS AT LOW TOTAL PRESSURESK.H. BECKER¹, B. ENGELHARDT, P. WIESEN*Physikalische Chemie/FB 9, Bergische Universität-Gesamthochschule Wuppertal,
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Rate constants for the reactions of CH(X²Π) with N₂, O₂, N₂O, H₂, D₂ and H were measured under pseudo-first-order conditions at 297 K and 2 Torr total pressure. CH(X²Π) radicals were generated by excimer laser photolysis (248 nm) of CH₂Br₂/Ar and CHClBr₂/Ar mixtures and detected by laser-induced fluorescence (LIF). The values obtained (cm³ s⁻¹) are: $k_{N_2} = (8.0 \pm 0.6) \times 10^{-14}$, $k_{O_2} = (5.1 \pm 0.3) \times 10^{-11}$, $k_{N_2O} = (6.9 \pm 0.9) \times 10^{-11}$, $k_{H_2} = (2.0 \pm 0.3) \times 10^{-12}$, $k_{D_2} = (1.7 \pm 0.4) \times 10^{-11}$ and $k_H = (1.4 \pm 0.5) \times 10^{-11}$.

1. Introduction

The methylidyne radical is one of the most prominent radicals involved in hydrocarbon combustion processes [1] as well as in planetary atmospheres [2] and interstellar clouds [3]. In hydrocarbon oxidations it is thought to be a precursor of soot particles [4,5]. The formation of chemions via the reaction with oxygen atoms [6] and the formation of electronically excited flame species, e.g. OH(A²Σ⁺) via the reaction CH+O₂→OH*+CO [7,8], are further examples of important CH reactions in hydrocarbon oxidations. In addition, the reaction of CH radicals with N₂ is considered as the main source for the "prompt" NO [9] in combustion systems. Because of the importance of the methylidyne radical in these different reaction systems, a knowledge of the rate constants for the reactions of CH radicals with different reactants is of great interest.

In 1967 Braun et al. [10] and in 1971 Bosnali and Perner [11] measured a few rate constants for CH reactions at room temperature. Between 1979 and

1986 several papers were published in which the temperature and pressure dependences of rate constants for the reactions of CH radicals with several molecules relevant to hydrocarbon combustion were determined. The present knowledge of CH kinetics was recently reviewed [12]. However, the reactions of methylidyne with other radicals have only been investigated for the reactions CH+O [13,14] and CH+N [13]; product analyses were carried out only for the reactions CH+NO and CH+O₂ [15,16]. More recently, Anderson et al. [17] have studied the kinetics of CH(X²Π) reactions in a flow tube using the reaction of alkali atoms with bromoform as the source of methylidyne radicals. Despite the numerous investigations large discrepancies exist for some of the rate constants given in the literature. In the present work rate constants for the reactions of CH radicals with O₂, N₂, N₂O, H₂, D₂ and H atoms were measured at 297 K and a total pressure of 2 Torr using a pulsed UV laser photolysis-laser-induced fluorescence (LIF) technique. One of the aims of the present work was to improve the data needed for modeling low-pressure hydrocarbon atom flames.

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2. Experimental

All measurements were carried out at room temperature in a black anodized cubic aluminum cell having a volume of 730 cm³. CH radicals in their electronic ground state were generated by multiphoton dissociation of ≈ 1.5 mTorr CH₂Br₂ or ≈ 1 mTorr CHClBr₂, both diluted in argon to a ratio of 1/20, using a focused KrF excimer laser at 248 nm (Lambda Physik, EMG 102, 15 ns pulse width, maximum energy 300 mJ/pulse). The excimer laser beam was focused by a quartz lens ($f=1000$ mm) through a system of several diaphragms into the center of the cell. The relative CH radical concentrations were monitored by LIF. In the case of CH₂Br₂ as the parent molecule methylidyne radicals were excited by a tunable nitrogen-pumped dye laser (Lambda Physik, K 300, maximum energy 20 μ J/pulse). The dye stilbene 3 was used in these experiments. With CHClBr₂ as the parent molecule methylidyne radicals were excited by a Nd³⁺:YAG-laser-pumped dye laser (Quantel TDL IV) frequency mixed with the 1064 nm line of the YAG laser (Quantel YG 481). The dye used in these experiments was pyridine 2. In order to minimize scattered light the dye laser beam was passed through a special light baffle similar to that used previously [18].

The fluorescence signal was monitored at right angles to the laser beams through a bandpass filter centered at 430 nm by a photomultiplier (1P28). The output of the photomultiplier was gated, integrated and averaged by a boxcar signal averager (Princeton Applied Research model 162) and recorded with a strip chart recorder or a microcomputer. The time delay between the photolysis and the probe laser pulse was varied between 0 and several hundred microseconds using a digital delay generator (BNC model 7010). The lasers were operated at a repetition rate of 30 or 10 Hz, respectively. All measurements were carried out in a slowly flowing gas mixture (flow < 0.5 m/s). Pressures were measured by capacitance manometers (MKS Instruments). The concentrations of the gases used were determined from their partial flows measured with calibrated flow meters (Rotameter). Most of the measurements were carried out at a total pressure of 2 Torr using argon as a buffer gas.

All gases employed in this work were from Messer

Griesheim and used without further purification. CH₂Br₂ (Merck, 99% purity) and CHClBr₂ (Alfa, 99% purity) were carefully degassed before use. Hydrogen atoms were generated by a microwave discharge in an H₂/Ar mixture. Their concentrations were calibrated by titration with NO₂.

3. Results and discussion

The relative CH(X² Π) concentrations were measured by LIF from the integrated intensity of the Q-branch of the A² $\Delta \rightarrow$ X² Π (0, 0) transition at 431.5 nm. Fig. 1 shows a typical semi-log plot of the relative CH concentration as a function of time after the 248 nm laser pulse for H₂ as reaction partner. For hydrogen and nitrogen as reactant gases an increase of the LIF intensity was observed (up to a factor of two compared to that with only argon present). This behaviour was not seen when other gases were added. The time profile of the CH signal did not show any increase at early times.

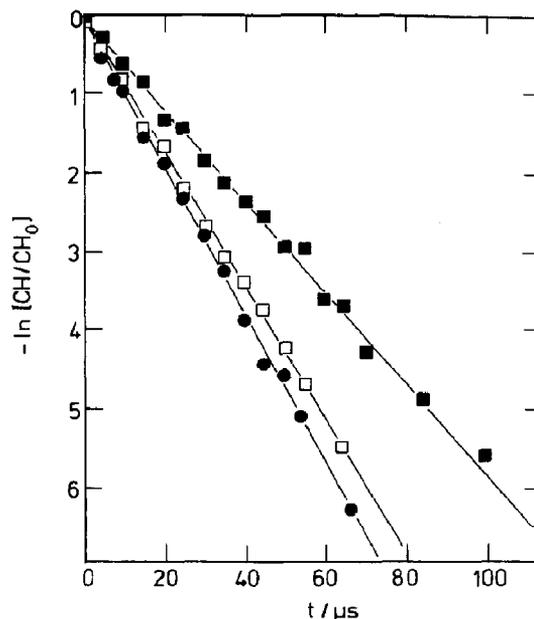


Fig. 1. Semi-log plot of CH decay after excimer laser photolysis of 1.5 mTorr CHClBr₂ with a focused laser beam in the presence of different H₂ concentrations, total pressure 2 Torr argon. ■, 0 mTorr H₂; □, 404 mTorr H₂; ●, 694 mTorr H₂.

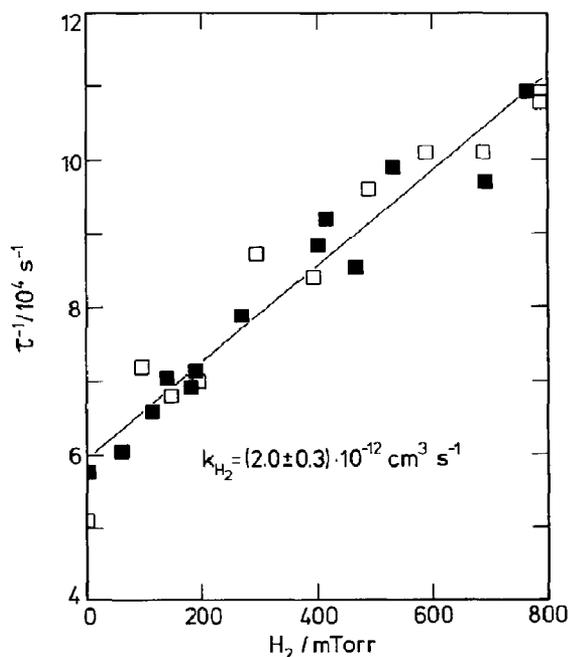


Fig. 2. Plot of first-order decay constants of CH radicals versus the concentration of molecular hydrogen at 2 Torr total pressure. \square , CH_2Br_2 as CH source, buffer gas: argon; \blacksquare , CHClBr_2 as CH source, buffer gas: argon.

From the slopes of the decay curves with different concentrations of the reactants bimolecular rate constants were derived for the depletion of CH as shown in fig. 2 for H_2 as reactant. For the evaluation of the rate constant of the $\text{CH} + \text{H}$ reaction the reaction of undissociated H_2 which was always present in the reaction system due to the method of H atom generation had to be considered. Table 1 summarises the rate constants measured in this work in comparison with literature values.

3.1. Reaction with O_2

The highly exothermic reaction of $\text{CH}(\text{X } ^2\Pi)$ radicals with O_2 is thought to be responsible for the OH^* chemiluminescence that can be observed in many hydrocarbon flames:

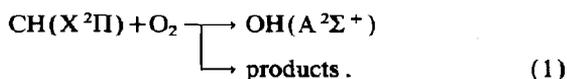


Table 1

Rate constants for the reactions of $\text{CH}(\text{X } ^2\Pi)$ radicals with selected species R at room temperature and a total pressure of 2 Torr

R	k ($10^{-11} \text{ cm}^3 \text{ s}^{-1}$)		Ref.
	this work ^{a)}	literature values	
O_2	5.1 ± 0.3	8.0 ± 3.0	[15]
		3.3 ± 0.4	[16]
		2.3 ± 0.5	[17]
		5.9 ± 0.8	[19]
		5.1 ± 0.5	[20]
		0.2 ± 0.02 ^{b)}	[21]
		0.43 ± 0.04 ^{c)}	[21]
N_2	0.008 ± 0.0006	0.003 ^{d)}	[22]
		0.005	[23]
		0.0078 ± 0.0001	[24]
N_2O	6.9 ± 0.9	4.2 ± 0.7	[17]
		7.8 ± 1.4	[23]
		0.58	[24]
H_2	0.2 ± 0.03	0.1	[10]
		0.063 ± 0.012	[17]
		0.02 ^{d)}	[25]
		0.065 ± 0.016 ^{e)}	[26]
		0.09 ± 0.03 ^{e)}	[26]
D_2	1.7 ± 0.4	—	
H	1.4 ± 0.5	$0.2\text{--}0.6$ ^{e)}	[27]
		16 ^{e)}	[28]
		1.21 ^{e)}	[29]
		2.9 ^{e)}	[30]
		4 ^{e)}	[31]

^{a)} The uncertainties represent 1σ and are based on the statistical precision of the least-squares fit only.

^{b)} Total pressure 10 Torr, measured for $\text{CH}(\text{X } ^2\Pi, v=0)$.

^{c)} Total pressure 10 Torr, measured for $\text{CH}(\text{X } ^2\Pi, v=1)$.

^{d)} Extrapolated from k_0 and k_∞ given in ref. [22] and ref. [25], respectively.

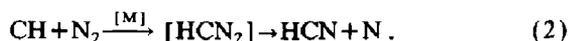
^{e)} See text.

The OH^* chemiluminescence in the 305–319 nm region occurring from the above reaction was investigated recently by Lichtin et al. [15] and Messing et al. [16], who found the reaction to be independent of pressure. These authors obtained rate constants for the overall reaction (1) of $(8 \pm 3) \times 10^{-11}$ and $(3.3 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$, respectively. These results and the values of $(5.9 \pm 0.8) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ determined by Butler et al. [19] and of $(5.1 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ determined by Berman et al. [20] are in good agreement with the value of

$(5.1 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ of the present work. However, the values obtained by Duncanson and Guillory [21] of 2.1×10^{-12} and $4.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for the vibrational levels $v''=0$ and $v''=1$, respectively, are much smaller.

3.2. Reaction with N_2

The reaction of CH with N_2 seems to be one of the best studied reactions in CH chemistry [10,11,19,21–24]. This reaction is considered to be responsible for the "prompt" NO formation in high temperature combustion systems [9] forming a complex followed by the oxidation of the products:



In the present measurements the addition of N_2 to the reaction system caused a significant increase of the CH LIF signal. A comparison of the energy of the $v''=1$ levels of $\text{CH}(X^2\Pi)$ and $\text{N}_2(X^1\Sigma_g^+)$ exhibits a reasonably good resonance between the states; this may result in a fast vibrational relaxation of any $\text{CH}(v \geq 1)$. The reaction of CH radicals with molecular nitrogen was first measured by Braun et al. [10]. The rate constant obtained by these authors was $7.2 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at 300 K and a total pressure of about 10 Torr.

Measurements by Berman and Lin [22] showed that the reaction is pressure and temperature dependent over a wide range. From the k_0 and k_∞ values obtained in their study a rate constant of $3 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ was extrapolated for a total pressure of 2 Torr. Wagal et al. [23] reported a value of $5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at 2 Torr total pressure, which is in reasonable agreement with the present value of $(8.0 \pm 0.6) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$.

Thermodynamically reaction (2) is endothermic by 15.4 kJ/mol, which can explain the rather slow rate constant. Reaction (2) should be forbidden as it does not follow spin conservation. The spin conservation rule generally holds for simple abstraction reactions. Because of the pressure dependence of reaction (2) Butler et al. [19] proposed a long-lived complex $[\text{HCN}_2]$ as an intermediate which can undergo multiple crossings between several potential energy surfaces of different spin configurations.

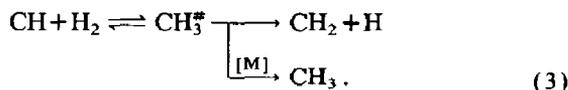
3.3. Reaction with N_2O

The value $(6.9 \pm 0.9) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ obtained for the rate constant of the reaction of $\text{CH}(X^2\Pi)$ radicals with N_2O is in good agreement with the value of $(7.8 \pm 1.4) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ measured by Wagal et al. [23], who used a laser photolysis/LIF technique in their experiments similar to that applied in the present study. On the other hand, Anderson et al. [17] and Nesbitt [24] have measured rate constants that are factors of 2 and an order of magnitude smaller, respectively, than the present value. Both groups used a conventional fast-flow reactor in combination with LIF detection of the $\text{CH}(X^2\Pi)$ radicals; however, the CH radical sources were different.

Compared with other radical + N_2O reactions, e.g. the reaction with $\text{O}(^1\text{D})$ [32] or $\text{C}(^3\text{P})$ [33], the rate constant for the reaction with $\text{CH}(X^2\Pi)$ radicals is not unusually fast. Thermodynamic considerations show that the reaction might lead to several different reaction products. Wagal et al. [23] proposed NO, HCN and N_2 as the most probable products. Accordingly, the reaction of CH radicals with N_2O opens another reaction path for the formation of nitric oxide in combustion systems. Because N_2O is a pollutant formed in the combustion of fossil fuels [34–37] it might be necessary to include the above reaction in modeling schemes of combustion systems.

3.4. Reaction with H_2 and D_2

The reaction of CH radicals with H_2 , which was found to be pressure dependent over a wide pressure range [25,38], has two available reaction channels, a slightly endothermic abstraction and an addition:



Very recently Zabarnick et al. [26] investigated the temperature dependence of this reaction in the temperature range 372 to 675 K at a total pressure of 100 Torr. They found that the production of CH_3 radicals dominates at temperatures < 300 K, whereas at temperatures > 400 K the formation of CH_2 radicals becomes more important.

As we observed in the $\text{CH} + \text{N}_2$ system the maxi-

imum of the LIF signal from CH typically increased by a factor of two when H₂ was added. The increase in the CH concentration cannot be attributed to a rapid generation of CH by reaction of a photolysis fragment (carbon atoms) with hydrogen, as proposed by Berman and Lin [25] because the same effect was observed when N₂ was added as reactant. It seems likely that the increase has to be attributed to relaxation processes as in the CH+N₂ reaction system. Very recently Nishiyama et al. [39] found that the CH(X²Π, v''=1) level rapidly relaxes to v''=0 by collisions with H₂. A comparison of the present rate constant with literature values (table 1) shows some discrepancies. The value of Anderson et al. [17] is a factor of three smaller than the present value. From the k₀ and k_∞ values obtained by Berman and Lin [25] in their investigation of the pressure dependence of the reaction of CH+H₂ over the range from 25 to 600 Torr a rate constant of 2×10⁻¹³ cm³ s⁻¹ was extrapolated for 2 Torr total pressure. However, because k₀ and k_∞ are associated with large error limits the extrapolated rate constant should only be considered as a rough estimate. From a more recent study of the temperature dependence of reaction (4) Zabarnick et al. [26] obtained an Arrhenius expression for the abstraction channel of (3) of k=(2.38±0.31)×10⁻¹⁰ exp[(-1760±60)/T] cm³ s⁻¹. The rate constant of (6.5±1.6)×10⁻¹³ cm³ s⁻¹ calculated for a temperature of 297 K can be compared with the present rate constant for the reaction of CH radicals with H₂ because at 2 Torr total pressure the abstraction channel of reaction (3) should be the dominant reaction path. Using the Arrhenius expression obtained from a transition state theory (RRKM) calculation by Zabarnick et al. [26] a rate constant of (9±3)×10⁻¹³ cm³ s⁻¹ was calculated. Similar to the previous findings of Berman and Lin [25] the rate constant of the reaction of CH radicals with D₂ was found to be 8.5 times larger than that of CH+H₂. Berman and Lin [25] explained the large difference between these two rate constants by a reaction mechanism involving a rapid isotopic exchange, e.g.



However, no kinetic data are available for the reaction CH+D₂ at a total pressure of 2 Torr which

can be compared with our experimental value of (1.7±0.4)×10⁻¹¹ cm³ s⁻¹.

3.5. Reaction with hydrogen atoms

The reaction of hydrogen atoms with CH(X²Π) radicals was predicted to form ground state carbon atoms via [8]



Reaction (5) is exothermic by 97 kJ/mol. Another possible path could be the addition of atomic hydrogen leading to methylene radicals:



In this work, the overall rate constant for the reaction of CH+H was determined over a pressure range from 2 to 12 Torr. A rate constant of (1.4±0.5)×10⁻¹¹ cm³ s⁻¹ for the reaction of CH(X²Π)+H was obtained independent of the total pressure within the experimental error limit (see fig. 3).

Only a few data derived from theoretical calcu-

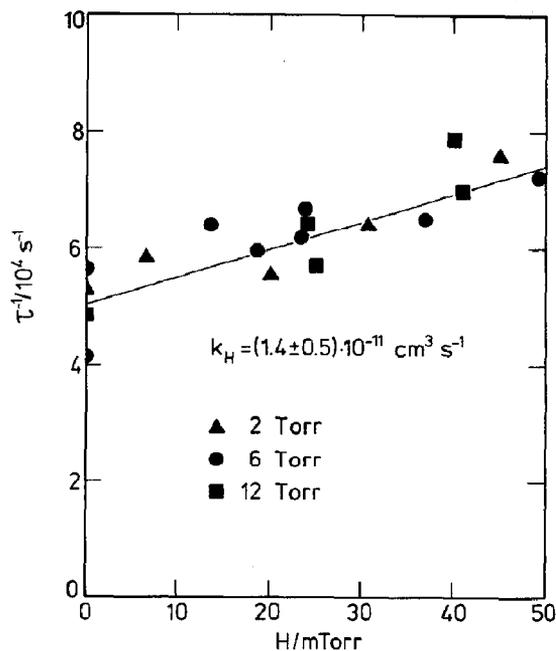


Fig. 3. Plot of first-order decay constants of CH radicals versus the concentration of atomic hydrogen at different total pressures: ▲, 2 Torr argon; ●, 6 Torr argon; ■, 12 Torr argon.

lations or indirect observations in different reaction systems are available for comparison with the present result. Meuser [27], who measured the formation of CH($X^2\Pi$) radicals in the reaction of C_2O radicals with atomic hydrogen at 2 Torr total pressure, estimated a rate constant of between 2×10^{-12} and 6×10^{-12} $cm^3 s^{-1}$ for the reaction $CH(X^2\Pi) + H$. Peeters and Vinckier [28] published an upper limit of 1.6×10^{-10} $cm^3 s^{-1}$ for the destruction of CH radicals by hydrogen atoms at a temperature of 2000 K in the $CH_4 + O$ and $C_2H_4 + O$ flames, which is one order of magnitude larger than the present value. Lange et al. [29] estimated a rate constant of 1.2×10^{-11} $cm^3 s^{-1}$ from self-absorption experiments on CH generated in a pulsed discharge of methane, which agrees well with our value. Eschenroeder and Lord [30] calculated a rate constant of 2.9×10^{-11} $cm^3 s^{-1}$ at 4500 K with respect to the role of this reaction in rocket exhausts. More recently Murrell and Dunne [31] carried out quasi-classical trajectory calculations for the triplet ground-state surface of methylene in order to evaluate the rate constant for reaction (5) over the temperature range from 1000 to 2000 K. They determined a rate constant of 4×10^{-11} $cm^3 s^{-1}$ almost independent of temperature. All these previous values are dependent on several assumptions and can only be considered as rough estimates.

Our experimental results support reaction (5) as a source of carbon atoms in hydrocarbon flames because

(1) no dependence of the rate constant on the total pressure was observed (reaction (6) should have a pressure dependence), and

(2) the calculated third-order rate constant of 10^{-28} $cm^6 molecule^{-2} s^{-1}$ would be unreasonably large for the recombination step, reaction (6), at 2 Torr.

4. Conclusions

In conclusion, we have obtained absolute rate constants for the reaction of CH($X^2\Pi$) radicals with O_2 , N_2 , N_2O , H_2 , D_2 and H atoms at 297 K and a total pressure of 2 Torr using a laser flash photolysis-LIF technique. For the reactions of ground-state CH radicals with O_2 and N_2 the present rate constants are

in good agreement with most literature data. However, the rate constants for the reactions of CH radicals with N_2O , H_2 and D_2 obtained from fast-flow studies of the CH kinetics are all smaller than those obtained from laser photolysis/LIF experiments.

The rate constant for the reaction $CH + H$ was determined for the first time. The experimental results support the formation of ground-state carbon atoms as reaction product although carbon atoms were not directly detected in the system.

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