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Temperature dependence of the reactions of CH radicals with NO, NH₃ and N₂O in the range 200–1300 K

K.H. Becker, B. Engelhardt, H. Geiger, R. Kurtenbach and P. Wiesen¹

*Physikalische Chemie / Fachbereich 9, Bergische Universität-Gesamthochschule Wuppertal,
Postfach 100127, W-5600 Wuppertal 1, Germany*

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Bimolecular rate constants for the reactions of CH($X^2\Pi$) radicals with nitric oxide, ammonia and nitrous oxide were measured under pseudo-first-order conditions at 4 Torr total pressure, as a function of temperature in the range 300–1300 K for the CH + NO and CH + NH₃ reaction and in the range 200–1250 K for the CH + N₂O reaction. CH radicals were generated by excimer laser photolysis of CHClBr₂/Ar mixtures and were detected by laser-induced fluorescence. The rate constant of the reaction CH + NO was found to be independent of temperature. The measured rate constants of the reactions CH + N₂O and CH + NH₃ exhibit negative temperature dependences which are described by the following Arrhenius equations (with E_A in units of kJ/mol): $k_{CH+N_2O}(T) = (3.09 \pm 0.07) \times 10^{-11} \exp[(2.14 \pm 0.08)/RT] \text{ cm}^3 \text{ s}^{-1}$, $k_{CH+NH_3}(T) = (7.23 \pm 0.17) \times 10^{-11} \exp[(2.64 \pm 0.10)/RT] \text{ cm}^3 \text{ s}^{-1}$ and $k_{CH+NO}(T) = (1.87 \pm 0.06) \times 10^{-10} \exp[(0.00 \pm 0.15)/RT] \text{ cm}^3 \text{ s}^{-1}$. All reactions were found to be very fast, with rate constants close to the gas kinetic limit. The negative temperature dependences for the reactions CH + N₂O and CH + NH₃ are in accord with an addition/decomposition mechanism and are similar to those observed for the reactions of CH radicals with saturated and unsaturated hydrocarbons.

1. Introduction

CH radicals in different electronic states are important reactive intermediates occurring in, for example, hydrocarbon combustion and planetary atmospheres [1]. Numerous experiments on CH radical kinetics have been carried out during the last few years and CH($X^2\Pi$) kinetics has been the subject of a recent review [2].

Of particular interest are reactions of CH radicals with molecular nitrogen, nitrogen oxides (NO, NO₂, N₂O) and ammonia because of the key role CH radicals play in NO_x formation and destruction in flames [3]. Fenimore [4] was the first to propose that N₂ is converted to NO by reaction with CH in the flame front leading primarily to HCN which can be further oxidized to NO,



Under certain conditions such as “low” temperature, a rich mixture and a short residence time in the

combustor this so-called “prompt NO” formation can be the dominant source of NO_x in flames. Recently, the kinetics and mechanism of the CH + N₂ reaction have been studied over a large temperature range by several authors [5–7].

CH radicals can, however, also react rapidly with NO thus allowing cycling of NO to other nitrogen-containing species, which might be converted to N₂ and thus serve as a mechanism for reduction of NO. Although no product measurements are available, Miller and Bowman [8] suggested HCN and oxygen atoms as the single products of the CH + NO reaction.

For modeling nitrogen chemistry in lean flames under relatively low-temperature conditions the reaction of CH radicals with N₂O, which can serve as an intermediate for NO formation [9], is of particular importance. Since ammonia is used for reducing NO in combustors in the so-called “thermal deNO_x” process, the kinetics of the CH + NH₃ reaction is also of interest for modeling combustion processes.

The kinetics of CH radicals with NO has been studied by several authors [10–13], however, the temperature dependence has only been investigated

¹ To whom correspondence should be addressed.

over a limited temperature range. The reactions $\text{CH} + \text{N}_2\text{O}$ and $\text{CH} + \text{NH}_3$ have been studied in the temperature range 298–670 K by Zabarnick and co-workers [14,15] at 100 Torr total pressure.

In continuation of our work on CH radical kinetics, the reactions of $\text{CH}(X^2\Pi)$ radicals with nitrogen containing reactants, namely NO, NH_3 and N_2O have been investigated over a large temperature range at 4 Torr total pressure using a pulsed UV laser photolysis (LP)–laser-induced fluorescence (LIF) technique.

2. Experimental

The experimental setup used in the present work was similar to that employed previously in our laboratory [1,5,16]. Briefly, the focused 248 nm radiation of a Lambda Physik EMG 102 excimer laser with a pulse energy of 150 mJ operating at 10 Hz was used to generate CH radicals by multiple photon dissociation of CHClBr_2 which was diluted in Ar by a ratio of $\approx 1:200$. Relative $\text{CH}(X^2\Pi)$ concentrations were monitored by LIF using the Q-branch of $A^2\Delta \rightarrow X^2\Pi$ transition at 431.4 nm. The probe laser was a Lambda Physik system comprising a FL 3001 dye laser pumped by an EMG 102 excimer laser. For monitoring CH radicals the dye laser was operated with stilbene 3 (Radiant Dyes) in methanol yielding typical pulse energies of 1–2 mJ.

Depending on the temperature range two different reaction cells were used. The reaction cell which was used in the range 200–900 K consisted of a stainless-steel cylinder through which the photolysis and the probe laser beams counterpropagated. In the experiments carried out at elevated temperatures the cell was heated by means of a Ni/Cr (80/20) resistive wire. For studying reactions below room temperature, a coolant fluid was circulated through a jacket surrounding the reaction cell. For temperatures above 900 K a reactor comprising a stainless-steel cylinder with an inner ceramic cylinder was used. The ceramic cylinder was heated by means of a tantalum resistive wire. Details of the high-temperature reactor will be given in a separate paper [17]. The temperature in both cells was measured by shielded, calibrated thermocouples and kept constant during the experiments to better than ± 1.5 K.

The CH fluorescence was observed at right angles to the laser propagation through a continuous band filter before reaching a gating microchannel plate photomultiplier (Hamamatsu R2024U-07) which was used to reduce scattered light from the dye laser. The photomultiplier output was integrated by a boxcar averager (SRS model SR 250), digitized and analyzed by an ATARI MegaST microcomputer. The time delay between the photolysis laser and the probe dye laser pulse was varied from zero to several hundred microseconds by a digital delay generator (BNC 7010).

All reactions were investigated under pseudo-first-order conditions with reactant concentrations at least a hundred times larger than the CH precursor CHClBr_2 . All measurements were carried out in slowly flowing gas mixtures with flow rates < 0.5 m s^{-1} . The concentrations of the gases were determined from their partial flows measured with calibrated flowmeters (Tylan FM 360).

All gases employed in this work were supplied by Messer-Griesheim and were used without further purification, except for NO, which was passed through a cooling trap kept at 195 K in order to remove small NO_2 impurities. The purities of the gases used were 99.998% (Ar), 99.990% (N_2O), 99.8% (NO) and 99.98% (NH_3). CHClBr_2 (Alfa, 99% purity) was carefully degassed before use.

3. Results and discussion

From the LIF measurements, relative CH radical concentrations were determined as a function of the reaction time. As shown in fig. 1, in the absence of the reactant the LIF intensity increased at very short delay times and then decayed exponentially. The CH decay was mainly caused by reactions with CHClBr_2 and the photolysis products and also by diffusion out of the observation zone. The initial rise in the CH concentration was probably caused by vibrational relaxation into the vibrational ground state of CH. The addition of reactants caused a more rapid vibrational relaxation. In order to exclude any influence of relaxation on the results, the decay curves were analyzed after the initial rise of the fluorescence signal was complete.

For a CHClBr_2 concentration of 0.1 mTorr, which

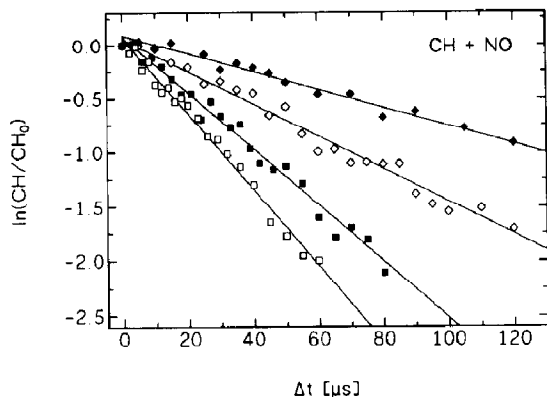


Fig. 1. Semilog plot of CH decay after excimer laser photolysis of 1.2×10^{12} molecules cm^{-3} CHClBr_2 in the presence of different NO concentrations (10^{13} molecules cm^{-3}) at $T=586$ K: (\blacklozenge) 0; (\diamond) 3.2; (\blacksquare) 10.2; (\square) 14.4.

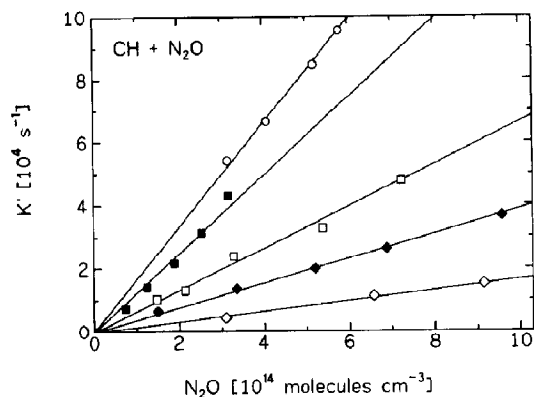


Fig. 2. Plot of pseudo-first-order decay constants K' of CH radicals versus the concentration of N_2O : (\circ) 199 K; (\blacksquare) 239 K; (\square) 298 K; (\blacklozenge) 438 K; (\diamond) 884 K.

was typically used, the CH decay could be monitored over a period of about 1 ms or 6 lifetimes. By plotting the natural logarithm of the relative CH concentration as a function of reaction time pseudo-first-order decay constants, K , were calculated from the slope of the individual straight line plots which were obtained for different reactant concentrations. The K values increased proportionally with the concentration of the added reactant, as shown in fig. 1 and taking the $\text{CH} + \text{NO}$ reaction as an example.

The bimolecular rate constants, k , for a given temperature were then obtained by plotting corrected pseudo-first-order rate constants, K' , as a function of the reactant concentration, as shown in fig. 2 and

taking the $\text{CH} + \text{N}_2\text{O}$ reaction as an example once again. The K' values were obtained by subtracting the decay constants, which were obtained in the absence of the reactants, from the corresponding K values.

3.1. Reaction with NO

The $\text{CH} + \text{NO}$ reaction is very important for modeling nitrogen chemistry in flames. Along with other CH_x radicals this reaction provides a pathway for NO destruction and recycling of HCN in combustion processes. It was proposed by Miller and Bowman [8] that HCN and oxygen atoms are the single products of this reaction. However, Bozelli and co-workers [18] recently carried out QRRK calculations of the $\text{CH} + \text{NO}$ reaction which imply that the product distribution might be more complex than suggested by Miller and Bowman [8].

In the present work, the $\text{CH} + \text{NO}$ reaction was investigated in the temperature range 300–1300 K at 4 Torr total pressure. The bimolecular rate constants obtained are shown in fig. 3 and are summarized in table 1 with error limits representing a 90% confidence interval. For the individual temperatures the given rate constants were calculated as weighted means from four independent measurements with at least five different NO concentrations. In the investigated temperature range the reaction is independent of temperature, within experimental error, with a rate constant of $(1.9 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$. Using

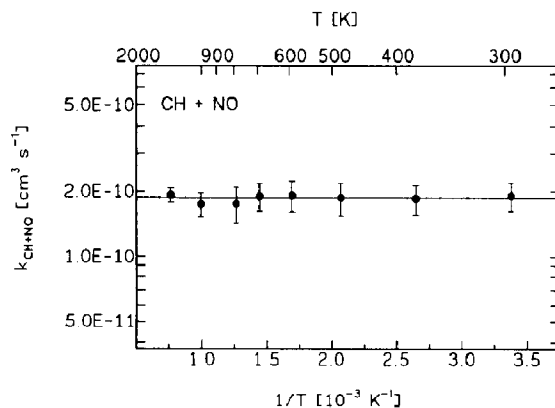


Fig. 3. Arrhenius plot of the bimolecular rate constant $k_{\text{CH}+\text{NO}}$ versus $1/T$ for the reaction $\text{CH} + \text{NO} \rightarrow \text{products}$. The solid line is a weighted, linear least-squares fit to the data.

Table 1

Bimolecular rate constants for the reaction $\text{CH} + \text{NO}$ measured as a function of temperature at 4 Torr total pressure (error limits represent a 90% confidence interval)

T (K)	$k_{\text{CH}+\text{NO}}$ ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)
298	1.90 ± 0.29
378	1.84 ± 0.29
483	1.86 ± 0.32
590	1.91 ± 0.31
692	1.89 ± 0.28
789	1.75 ± 0.33
1004	1.74 ± 0.22
1311	1.92 ± 0.14

the simple Arrhenius expression, $k = A \exp(-E_A/RT)$, the rate constant is described by

$$k_{\text{CH}+\text{NO}}(T) = (1.87 \pm 0.06) \times 10^{-10}$$

$$\times \exp(0.00 \pm 0.15/RT) \text{ cm}^3 \text{ s}^{-1},$$

with E_A in units of kJ/mol.

The measured rate constants from the present study are in excellent agreement with literature data. Berman et al. [11], who studied the reaction in the temperature range 297–673 K at a total pressure of 100 Torr, found a rate constant of $(1.9 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, independent of temperature. More recently, Hanson and co-workers [12] studied the $\text{CH} + \text{NO}$ reaction using the shock tube technique in the range 2570–3790 K and reported a rate constant of $(1.7 \pm 0.9) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, independent of temperature.

3.2. Reaction with NH_3

Bimolecular rate constants for the reaction of CH radicals with ammonia were measured at 4 Torr total pressure as a function of temperature in the range 300–1300 K. In order to avoid any complications due to NH_3 photolysis or pyrolysis it was carefully checked by LIF that under the conditions applied no NH or NH_2 radicals were formed. The rate constants listed in table 2 with error limits reflecting a 90% confidence interval were calculated as weighted means from four to six independent measurements with at least five different NH_3 concentrations. Fig. 4 shows the Arrhenius plot for the $\text{CH} + \text{NH}_3$ reaction from which the following Arrhenius expression was derived:

Table 2

Bimolecular rate constants for the reaction $\text{CH} + \text{NH}_3$ measured as a function of temperature at 4 Torr total pressure (error limits represent a 90% confidence interval)

T (K)	$k_{\text{CH}+\text{NH}_3}$ ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$)
296	2.01 ± 0.17
386	1.63 ± 0.08
491	1.44 ± 0.12
590	1.26 ± 0.07
710	1.11 ± 0.13
818	1.07 ± 0.10
1028	0.96 ± 0.12
1290	0.91 ± 0.09

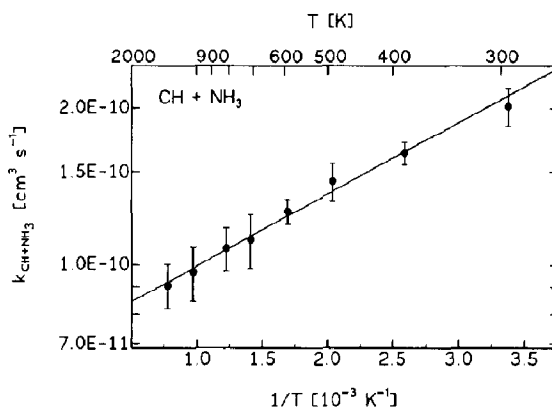


Fig. 4. Arrhenius plot of the bimolecular rate constant $k_{\text{CH}+\text{NH}_3}$ versus $1/T$ for the reaction $\text{CH} + \text{NH}_3 \rightarrow \text{products}$. The solid line is a weighted, linear least-squares fit to the data.

$$k_{\text{CH}+\text{NH}_3}(T) = (7.23 \pm 0.17) \times 10^{-11}$$

$$\times \exp[(2.64 \pm 0.10)/RT] \text{ cm}^3 \text{ s}^{-1},$$

with E_A in units of kJ/mol.

The activation energy and the A factor from the present work can be compared with those from Zabarnick et al. [15] who reported a negative activation energy of $-1.91 \pm 0.25 \text{ kJ/mol}$ and an A factor of $(8.6 \pm 0.6) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

Thermodynamic considerations show that the reaction might lead to several different reaction products. It was proposed by Zabarnick et al. [15] that a H_2CNH_2 intermediate is formed by insertion of a CH radical into one of the N–H bonds of NH_3 . This highly excited intermediate can then rapidly decompose to form H_2CNH and a hydrogen atom. How-

ever, Safrany et al. [19] proposed HCN, H₂ and H as the most probable products. Thus, the reaction of CH radicals with NH₃ could open an additional reaction path for HCN formation in combustion processes if NH₃ is added, e.g. in the thermal deNO_x process.

3.3. Reaction with N₂O

Bimolecular rate constants for the reaction of CH radicals with N₂O were measured at 4 Torr total pressure as a function of temperature in the range 200–1250 K. Variation of the total pressure in the range 1–22 Torr did not affect the value of the measured rate constant. This result is in agreement with the measurements of Zabarnick et al. [14], who found the reaction to be pressure independent in the range 30–300 Torr. Under the experimental conditions applied in the present study no photolysis and/or pyrolysis problems were anticipated since N₂O does not absorb at 248 nm and thermal decomposition becomes important only for temperatures > 1300 K [20]. The rate constants listed in table 3 with error limits reflecting a 90% confidence interval

Table 3

Bimolecular rate constants for the reaction CH + N₂O measured as a function of temperature at 4 Torr total pressure (error limits represent a 90% confidence interval)

<i>T</i> (K)	<i>k</i> _{CH+N₂O} (10 ⁻¹¹ cm ³ s ⁻¹)
199	10.9 ± 0.3
204	11.4 ± 1.0
208	9.4 ± 1.2
240	9.0 ± 1.2
246	9.2 ± 0.4
273	8.1 ± 0.8
298	6.8 ± 0.7
332	7.1 ± 0.3
395	5.9 ± 0.3
396	6.2 ± 0.2
438	5.5 ± 0.1
440	5.7 ± 0.3
442	5.7 ± 0.2
484	5.1 ± 0.2
578	5.1 ± 0.4
639	4.8 ± 0.6
728	4.5 ± 0.4
890	4.5 ± 0.5
1050	3.9 ± 0.3
1255	3.7 ± 0.2

were calculated as weighted means from four to six independent measurements with at least five different N₂O concentrations. Fig. 5 shows the Arrhenius plot for the CH + N₂O reaction from which the following Arrhenius expression was derived:

$$k_{\text{CH+N}_2\text{O}}(T) = (3.09 \pm 0.07) \times 10^{-11} \\ \times \exp[(2.14 \pm 0.08)/RT] \text{ cm}^3 \text{ s}^{-1},$$

with *E*_A in units of kJ/mol.

The observed negative temperature dependence is in agreement with that of Zabarnick et al. [14]. However, the *A* factor of $(1.59 \pm 0.20) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ and the activation energy of $-4.3 \pm 0.4 \text{ kJ/mol}$ reported by these authors are nearly factors of two lower and higher, respectively, compared with the values from the present study.

Thermodynamic considerations show that the reaction might lead to several different reaction products. All reaction channels are characterized by highly negative reaction enthalpies. The observed pressure and temperature dependence is in agreement with an addition/decomposition mechanism similar to that proposed by Berman and Lin [21] for the reaction of CH radicals with hydrocarbons. Probably, the CH radical inserts itself into the N–N and/or N–O bond of N₂O forming an highly excited intermediate which can rapidly decompose. Wagal et al. [22] who investigated the reaction at room temperature proposed NO, HCN and N₂ as the most probable reaction products. Accordingly, the reaction of CH

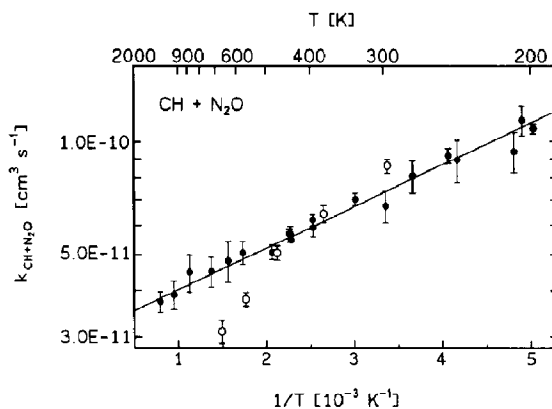


Fig. 5. Arrhenius plot of the bimolecular rate constant *k*_{CH+N₂O} versus 1/*T* for the reaction CH + N₂O → products; (●) this work and (○) Zabarnick et al. [14].

radicals with N_2O opens a possible additional reaction path for the formation of nitric oxide in flames. Since N_2O is a pollutant which is formed in the combustion of fossil fuels [23,24] it might be necessary to include the above reaction in modeling schemes of combustion systems.

4. Conclusion

In conclusion, absolute rate constants have been obtained for the reactions of $CH(X^2\Pi)$ radicals with NO , NH_3 and N_2O at 4 Torr total pressure in the temperature range 300–1300 K for the $CH+NO$ and $CH+NH_3$ reactions and in the range 200–1250 K for the $CH+N_2O$ reaction. The $CH+NO$ reaction was found to be temperature independent with a bimolecular rate constant which is in excellent agreement with literature data. The reactions $CH+NH_3$ and $CH+N_2O$ exhibit negative temperature dependences. However, the activation energies for both reactions obtained from the present study are significantly higher and lower, respectively, than literature values.

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