Kinetics of the Reaction $CH + N_2 \xrightarrow{[M]} Products in$ the Range 10–620 torr and 298–1059 K

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ABSTRACT

The gas-phase reaction of CH(X²II) radicals with molecular nitrogen was studied in the temperature range 298–1059 K at total pressures between 10 and 620 torr. CH radicals were generated by excimer laser photolysis of CHC1Br₂ at 248 nm and were detected by laser-induced fluorescence. The investigated reaction shows a strong temperature and pressure dependence. At pressures of 20, 100, and 620 torr the Arrhenius plots exhibit a strong decrease of the rate constant with increasing temperature. The rate constant is well described by.

 $k_{(20 \text{ torr})} = (24 \pm 6) \times T^{-(5.25 \pm 0.05)} \times \exp[-(7.57 \pm 0.83)/RT] \text{ cm}^3 \text{ s}^{-1},$

 $k_{(100 \text{ torr})} = (107 \pm 25) \times T^{-(5.25 \pm 0.05)} \times \exp[-(7.38 \pm 0.83)/RT] \text{ cm}^3 \text{ s}^{-1},$

 $k_{(620 \text{ torr})} = (1467 \pm 350) \times T^{-(5.48 \pm 0.05)} \times \exp[-(7.82 \pm 1.00)/RT] \text{ cm}^3 \text{ s}^{-1},$

with E_0 in kJ/mol. The pressure dependence was studied at temperatures of 298, 410, 561, and 750 K. The rate constants for each temperature were fitted by the Troe formalism. From the calculated values of k_0 and k_{∞} , the Arrhenius expressions,

$$k_0 = (1.1 \pm 0.2) \times 10^{-21} \times T^{(3.5 \pm 0.3)} \times \exp[-(6.4 \pm 0.5)/RT] \text{ cm}^6 \text{ s}^{-1}$$
 and
 $k_x = (1.9^{+0.3}_{-0.2}) \times 10^{-12} \times \exp[(3.6 \pm 0.4)/RT] \text{ cm}^3 \text{ s}^{-1},$

were obtained with $E_0(k_0)$ and $E_A(k_x)$ in units of kJ/mol. Within the range of 298-750 K the temperature dependence of the broadening factor is well described by $F_c = 0.029 + (173.3/T)$. © 1996 John Wiley & Sons, Inc.

In hydrocarbon combustion, the reaction of CH radi-

INTRODUCTION

In hydrocarbon combustion, the reaction of CH radicals with molecular nitrogen is the initial step of the formation of so called "prompt" NO [1-3]. Nitrogen oxides are probably the most important pollutants

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formed by combustion. Accordingly, several experiments have been carried out to study the kinetics of the reaction of CH radicals with molecular nitrogen in detail. Wagal and co-workers [4] found the CH + N_2 reaction to be pressure dependent in the range 10–100 torr at room temperature. The first detailed study of the CH + N_2 reaction was carried out by Berman and Lin [5]. The authors investigated the title reaction as a function of total pressure at room temperature and as a function of temperature at 100 torr total pressure. From their results, they proposed a reaction mechanism with two pathways,

$$CH(X^2II) + N_2 \implies [HCN_2]^{\#}$$

HCN + N(
4
S) (1a)
[M] HCN₂ (1b)

an addition channel (1b), which occurs at lower temperatures, and an abstraction reaction (1a), which becomes the dominant pathway at higher temperatures. These authors reported a rapid decrease of the bimolecular rate constant with increasing temperature at 100 torr in the temperature range 297-675 K, which is in agreement with the addition channel (1b). Subsequently, the pressure and temperature dependence of the CH + N₂ reaction was investigated in the low temperature regime (<1100 K) by other groups [6-8]. These experiments verified the negative temperature dependence of the rate constant in this temperature regime, as expected for a recombination reaction. Very recently, Balla and Castleton [9] reported a steady decrease of the rate constant for temperatures up to 1500 K.

Experiments, which were carried out at combustion temperatures using, e.g., the shock tube method [10-13] showed a positive temperature dependence of the rate coefficient, which is in agreement with the abstraction (1a).

Due to its importance in combustion chemistry, the CH + N₂ reaction has also become the subject of detailed theoretical studies [14-20] in the last few years. Manaa and Yarkony [14-16] were the first to characterize the hypersurface in the doubletto-quartet crossing region of the CH + N₂ system. Subsequent extensive ab initio calculations by Martin and Taylor [17], Walch [18], and Seideman [19,20] together with the experimental data outlined above led to the following reaction scheme,

$$CH(X^{2}II) + N_{2} \approx [HCN_{2}]^{*}_{C_{2\nu}} \longrightarrow HCN + N(^{4}S)$$
$$[HCN_{2}]^{*}_{dative}$$
$$\downarrow^{[M]}_{HCN_{2}}$$

An important aspect of the theoretical calculations was the characterization of an additional local minimum on the doublet surface of the reaction system which corresponds to the dative structure in the above reaction scheme and does not lead to the formation of HCN + N. Since this minimum can be apparently accessed at much lower energies Seideman and Walch [19] concluded that the negative temperature dependence which was observed in the low temperature regime (<1100 K) experiments resulted in the formation and stabilization of the datively bound complex rather than the $C_{2\nu}$ structure in the above reaction scheme. However, the details of the temperature and pressure dependencies of the rate constant and the activation energy of the $CH + N_2$ reaction remain controversial.

In order to complete knowledge about the kinetics of the CH + N₂ reaction, in the present paper bimolecular rate constants were measured over wide temperature and pressure ranges, namely 298-1059 K and 10-620 torr. The investigation of the temperature dependence of the limiting rate constants k_0 and k_{∞} yielded a set of parameters which allows the complete description of rate coefficients at any pressure or temperature within the investigated range. All experiments were carried out using the pulsed excimer laser photolysis (ELP)-laser-induced fluorescence (LIF) technique. The observed pressure dependencies at the given temperatures were analyzed by applying the Troeformalism [21-23].

EXPERIMENTAL

The experimental set-up used in the present work was similar to that employed previously in our laboratory [24-26]. Briefly, the focused 248 nm radiation of a Lambda Physik EMG 102 excimer laser with a pulse energy of 100 mJ operating at 10 Hz was used to generate CH radicals by multiphoton dissociation of CHClBr₂ which was diluted in Ar by a ratio of ≈ 1 :200. Relative CH(X²II) concentrations were monitored by LIF using the Q-branch of the $A^2 \Delta \rightarrow X^2 \Pi$ 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 Coumarin 120 (Radiant Dyes Chemie) in methanol, yielding typical pulse energies of 1.5-3 mJ.

The reaction cell used in the present work consisted of a stainless steel cylinder with an inner ceramic cylinder. The ceramic cylinder was heated by means of a tantalum resistive wire. The temperature in the reaction cell was measured by shielded, calibrated, and movable 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 and a gated microchannel plate photomultiplier (Hamamatsu R2024U-07) which was used to cut-off 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 was varied from zero to several hundred microsecond by means of a digital delay generator (BNC 7010).

The CH + N₂ reaction was investigated under pseudo-first-order conditions with N₂ concentrations at least a hundred times larger than the CH precursor CHClBr₂. 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). In all experiments argon was used as bath gas.

All gases employed in this work were supplied by Messer--Griesheim. The stated purities were 99.998% (Ar) and 99.9990% (N₂). In order to remove oxygen impurities, the gases were passed through Oxisorb cartridges (Messer-Griesheim). CHClBr₂ (Alfa, >99% purity) was carefully degassed before use.

RESULTS

From the LIF measurements, relative $CH(X^2\Pi)$ radical concentrations were measured as a function of the reaction time. As shown in Figure 1, in the absence of N₂ the LIF signal increased at very short reaction time and then decayed exponentially. The CH decay was mainly caused by reaction with CHClBr₂ and photolysis fragments. This is supported by the fact that the measured decay constants were strongly dependent on the CHClBr₂ concentration and the photolysis laser power. The initial rise in the CH concentration was probably caused by vibrational relaxation into the vibrational ground state of CH.

There is the possibility of an additional contribution to the observed CH decay from the diffusion of CH radicals out of the observation zone, which would be dependent on the concentration of added N_2 . However, experiments carried out previously in our laboratory [6], in which the carrier gas Ar was replaced stepwise by He, while all other experimental conditions were kept constant showed that for all



Figure 1 Semilog plot of CH decay after excimer laser photolysis of 5×10^{12} cm⁻³ CHClBr₂ in the presence of different N₂ concentrations (10^{17} cm⁻³): (\diamondsuit) 0; (\spadesuit) 1.35; (\Box) 2.33, (\blacksquare) 5.57; and (\bigcirc) 8.40. All data were obtained at 620 torr total pressure.

experiments the decay constants were identical within the experimental errors. Because of the very different diffusion coefficients of Ar and He a change in the pseudo-first-order decay by diffusion should be even more pronounced than in the case of N₂. The results support that diffusion effects are not important for the determination of the bimolecular rate constant k_{CH+N_2} .

For a CHClBr₂ concentration of 0.1 mtorr, which was typically used, the CH decay could be monitored over a period of about 1 ms or 6 lifetimes. The addition of N₂ caused a more rapid vibrational relaxation and a more rapid decay of CH radicals. 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 N₂ concentrations. The k' values increased proportionally with the concentration of added N₂, as shown in Figure 1.

The bimolecular rate constants k_{CH+N_2} for a given temperature were then obtained by plotting corrected pseudo-first-order rate constants $k'_{corr.}$ as a function of the N₂ concentration, as shown in Figure 2. The $k'_{corr.}$ values were obtained by subtracting the decay constants, which were measured in the absence of N₂, from the corresponding k' values.

During a series of experiments, large amounts of the bath gas argon were replaced by N₂. Since the CH + N₂ reaction is pressure dependent, the observed pseudo-first-order decay constants k' can be analyzed in terms of a third-order rate constant k_{CH+N_2+M} which is strongly dependent on the relative collision efficiencies of Ar and N₂. However, previous experimental work [5,6,8] has shown that the collision



Figure 2 Plot of pseudo-first-order decay constants $k'_{corr.}$ of CH radicals vs. the concentration of N₂: (\Box) 298 K; (\blacksquare) 410 K; (\bigcirc) 548 K; (\bullet) 640 K; (\diamondsuit) 741 K; and (\blacklozenge) 1017 K. All data were obtained at 620 torr total pressure.

efficiencies are equal for Ar and N_2 over the entire range of experimental conditions of the present study. Accordingly, the rate constants obtained in the present study are not affected by replacing Ar with N_2 .

Temperature Dependence

The bimolecular rate constant for the CH + N_2 reaction was measured at total pressures of 620, 100, and 20 torr as a function of temperature in the ranges 298–1016, 298–1059, and 410–752 K, respectively. The k-values obtained are shown in Figure 3 and are summarized in Table I together with literature data from Becker et al. [6]. The error limits represent a 90% confidence interval and reflect the statistical precision only. The rate constants listed in Table I are weighted means of at least four k-values which were determined in independent experiments using at least 6 different N₂ concentrations.

The Arrhenius plots for the different total pressures show negative temperature dependencies with a strong curvature. If one uses the three-parameter Arrhenius expression $k(T) = A \times T^n \exp(-E_0/RT)$, the rate constants at the given total pressures are well described by,

$$k_{(620 \text{ torr})} = (1467 \pm 350) \times T^{-(5.48 \pm 0.05)}$$

 $\times \exp[-(7.82 \pm 1.00)/RT] \text{ cm}^3 \text{ s}^{-1}$

 $k_{(100 \text{ torr})} = (107 \pm 25) \times T^{-(5.25 \pm 0.05)}$

$$\times \exp[-(7.38 \pm 0.83)/RT] \text{ cm}^3 \text{ s}^{-1},$$

 $k_{(20 \text{ torr})} = (24 \pm 6) \times T^{-(5.25 \pm 0.05)} \times \exp[-(7.57 \pm 0.83)/RT] \text{ cm}^3 \text{ s}^{-1},$

with E_0 in kJ/mol. These expressions were derived by weighted non-linear least squares procedures using the inverse squares of experimental errors of the rate constants as statistical weight.

Pressure Dependence

The pressure dependence of k_{CH+N_2} was investigated at temperatures of 298, 410, 561, and 750 K in the range 10-620 torr. Since the pressure dependence of the CH + N₂ reaction has been previously studied in detail at 298 K [4,5,7,8] in the present study only two additional measurements were carried out at total pressures of 100 and 620 torr.

The k-values obtained are listed in Table II and are shown in Figure 4 together with data from Wagal et al. [4], Berman and Lin [5], and Medhurst et al. [8]. The data for the individual temperatures were fitted to Troe's semiempirical equation [21-23],

$$k([\mathbf{M}], T) = \frac{k_0[\mathbf{M}]}{1 + k_0[\mathbf{M}]/k_{\pi}} \times F_c^{\left\{1 + \left[(1/N) \log(k_0[\mathbf{M}]/k_{\pi})\right]^2\right\}^{-1}}$$

with

$$N = 0.75 - 1.27 \log(F_c)$$

and are expressed by the solid lines in Figure 4. The values determined for the limiting rate constants k_0 and k_{∞} and the broadening factor F_c are given in Table III together with the calculated half pressures. The values of k_0 and k_{∞} were fitted by an iteration procedure, whereas the broadening factor was determined using the molecular parameters of the HCN₂ adduct which were calculated by Martin



Figure 3 Arrhenius plot of the bimolecular rate constant k_{CH+N_2} vs. 1/T at individual total pressures (torr): (**D**) 620; (**D**) 100; (**•**) 20, this work; and (**◊**) 20, Becker et al. [6]. The solid lines are weighted, nonlinear least-squares fits to a three-parameter Arrhenius expression to the corresponding data.

Table I Bimolecular Rate Constants for the Reaction $CH + N_2 \rightarrow Products$ as a Function of Temperature at Individual Total Pressures of 20, 100, and 620 torr; Error Limits Represent a 90% Confidence Interval

Pressure (torr)	Temperature (K)	k_{CH+N_2} (10 ⁻¹⁴ cm ³ s ⁻¹)	Reference
20	301	12.6 ± 0.5	[6]
	368	6.0 ± 0.2	[6]
	410	4.7 ± 0.5	
	472	2.9 ± 0.1	[6]
	563	1.9 ± 0.2	[6]
	572	1.7 ± 0.3	
	672	0.8 ± 0.1	
	673	1.5 ± 0.2	[6]
	752	0.6 ± 0.1	
	764	1.5 ± 0.2	[6]
	894	2.2 ± 0.3	[6]
100	298	59.9 ± 8.1	
	378	28.3 ± 2.3	
	408	17.4 ± 1.1	
	494	11.3 ± 3.2	
	560	8.0 ± 0.1	
	640	$4.6~\pm~0.8$	
	755	2.3 ± 0.5	
	1059	0.7 ± 0.1	
620	298	179.0 ± 2.9	
	357	99.0 ± 1.5	
	401	67.7 ± 2.8	
	446	49.7 ± 2.2	
	496	40.3 ± 4.4	
	550	27.1 ± 1.9	
	636	18.5 ± 1.3	
	742	10.0 ± 1.1	
	914	2.9 ± 0.5	
	1016	1.7 ± 0.4	

and Taylor [17] who used the complete active space self consistent field (CASSCF) optimization method. It should be pointed out that the given error limits are estimated values which were obtained by varying k_0 , k_{∞} , and F_c over a wide range. Probably the error limit of k_{∞} is much larger since all rate constants from the present study were measured well away from the high pressure limit. Accordingly, measurements of the rate constants at much higher total pressure would be very helpful for a better understanding of this important reaction.

From the data obtained for k_0 and k_{∞} at the individual temperatures, the following Arrhenius expressions describing the temperature dependencies of k_0 and k_{∞} were derived,

$$k_0 = (1.1 \pm 0.2) \times 10^{-21} \times T^{-(3.5\pm0.3)}$$
$$\times \exp[-(6.4 \pm 0.5)RT] \text{ cm}^6 \text{ s}^{-1},$$
$$k_x = (1.9^{+0.3}_{-0.2}) \times 10^{-12}$$
$$\times \exp[((3.6 \pm 0.4)/RT] \text{ cm}^3 \text{ s}^{-1},$$

with E_A and E_0 in kJ/mol.

The corresponding data are shown in the Figures 5 and 6, respectively. The solid lines are the result of weighted least-squares fits. The Arrhenius diagram of k_0 , Figure 5, is markedly curved, whereas the Arrhenius plot of k_{∞} , Figure 6, shows an excellent linear behavior within the given error limits.

The temperature dependence of the broadening factor F_c is well described by the expression $F_c = 0.029 + (173.3/T)$ within the investigated range of 298-750 K.

DISCUSSION

Temperature Dependence

The observed temperature dependence of the CH + N_2 reaction which was investigated in the present study at three individual total pressures is consistent with the reaction mechanism proposed by Berman and Lin [5]. It should be pointed out that the bimolecular rate constant k_{CH+N_2} decreased with increasing temperature for all investigated total pressures indicating that the addition channel (1b) dominates the

Table II Bimolecular Rate Constants for the Reaction $CH + N_2 \rightarrow Products$ as a Function of Total Pressure at Individual Temperatures of 298, 410, 561, and 750 K; Error Limits Represent a 90% Confidence Interval

$\overline{T \pm 2\sigma}$	Pressure	<i>k</i> _{CH · N2}
(K)	(torr)	$(10^{14} \text{ cm}^3 \text{ s}^{-1})$
298 ± 1	100	59.5 ± 8.1
	620	179.0 ± 2.9
410 ± 8	10	3.1 ± 0.3
	20	4.7 ± 0.4
	50	10.4 ± 0.9
	100	17.4 ± 1.1
	200	$26.2~\pm~2.0$
	300	34.2 ± 2.0
	450	55.8 ± 3.6
	621	67.7 ± 2.8
561 ± 7	20	1.7 ± 0.3
	50	4.7 ± 0.4
	100	8.0 ± 0.1
	200	12.8 ± 0.9
	300	14.8 ± 1.0
	450	23.1 ± 2.3
	620	27.1 ± 1.9
750 ± 6	20	0.6 ± 0.1
	50	1.3 ± 0.2
	100	2.3 ± 0.3
	201	4.3 ± 0.7
	298	6.6 ± 0.5
	449	8.3 ± 0.8
	620	10.0 ± 1.1



Figure 4 Comparison of the pressure dependencies of the bimolecular rate constant k_{CH+N_2} with Ar as bath gas at different temperatures: (•) 298 K, data of this work and literature data from ref. [4,5,8]; (O) 410 K, this work; (•) 561 K, this work; (\diamond) 750 K, this work; and (\blacksquare) Medhurst et al. [8], 750 K. The solid lines are the results of individual fits of the corresponding data to the expression of Troe [21–23].

reaction. This behavior is in disagreement with a previous study from our laboratory [6] in which an increase of the k-value for temperatures >673 K was reported at 20 torr total pressure. This discrepancy will be discussed below.

The temperature dependence of the CH + N₂ reaction was investigated for the first time at a total pressure of 620 torr in the range 298–1016 K. Using the temperature dependence reported by Dean et al. [11] and Lindackers et al. [12] who investigated the title reaction at temperatures >2300 K it can be estimated that even at 1000 K the influence of the abstraction on the k-values reported here is negligible, see Table IV. The values obtained for E_0 and the preexponential factor in the present study can be compared with those obtained at 100 torr and 20 torr total pressure. Because of the higher total pressure the measured rate coefficients are distinctly larger, and, consequently, also the preexponential factors.

At 100 torr total pressure the temperature dependence of k_{CH+N_2} shows also a steady decrease of the bimolecular rate constant with increasing temperature in the range 298-1059 K, indicating that under the experimental conditions the reaction is again dominated by the addition reaction (1b). The obtained k-values can be compared with the results of Berman and Lin [5] and Medhurst et al. [8], who investigated the $CH + N_2$ reaction as a function of temperature in 100 torr argon in the ranges 297-675 K and 298-1075 K, respectively. The k-values of the different studies are shown in Figure 7. Within the experimental errors the data from the present study are in good agreement with the rate coefficients given by Berman and Lin [5]. These authors used a simple Arrhenius equation for describing the temperature dependence of k_{CH+N} , in the range 297-675 K where the temperature dependence is almost linear. However, in the present study a three-parameter Arrhenius expression was used to describe the temperature dependence because the Arrhenius diagram was markedly curved in the temperature range 298-1059 K. The solid line in Figure 7 is the result of a nonlinear least-squares fit to the data reported here using a three-parameter Arrhenius expression.

The rate coefficients from the present study are significantly larger than those reported by Medhurst et al. [8]. The difference between the two sets of data is increasing from 30% at room temperature up to a factor of three at about 1060 K. Consequently, the Arrhenius equation reported by Medhurst et al. [8] exhibits a significantly smaller preexponential factor, while the values for the *n*-factor and the threshold energy E_0 are in good agreement within the experimental errors.

The temperature dependence of k_{CH+N_2} which was investigated in the present study at 20 torr total pressure in the range 410–752 K can be compared with previous work from our laboratory [6]. The two

Table III Limiting Rate Constants k_0 and k_{∞} , Obtained From a fit of the Measured Rate Constants to the Semiempirical Equation of Troe [21–23]. The Broadening Factors F_c were Calculated by an Algorithm of Troe. Using the Vibrational Frequencies of the HCN₂ Adduct given by Martin and Taylor [17]; Error Limits Represent a 90% Confidence Interval

Temperature (K)	k_0 (10 ⁻³² cm ⁶ s ⁻¹)	$\frac{k_{\infty}}{(10^{-12} \text{ cm}^3 \text{ s}^{-1})}$	F _c	$p_{1/2}$ (10 ³ torr)	Reference
298	27 ± 3	6.3 ± 1.3	_		[4]
298	28 ± 5	20 ± 10	_		[5]
298	18.0 ± 4.5	8.0 ± 4.0	0.60 ± 0.15	3.4	
410	12.0 ± 2.0	4.5 ± 2.0	0.47 ± 0.10	6.2	
561	6.6 ± 1.5	4.3 ± 1.5	0.34 ± 0.06	28.2	
750	3.5 ± 0.7	3.2 ± 1.0	0.25 ± 0.03	111.0	



Figure 5 Arrhenius plot of the termolecular rate constant k_0 for the reaction CH + N₂ $\xrightarrow{[M]}$ HCN₂ vs. 1/T. The solid line is a weighted, nonlinear least-squares fit to the data.

data sets are plotted in Figure 8 for comparison. In contrast to the findings from the previous study a continuous decrease of the rate constant was observed with increasing temperature, whereas Becker et al. [6] reported an Arrhenius plot which exhibits regions of negative and positive slope with a minimum at 673 K. From this result the authors concluded that above 673 K the abstraction (1a) leading to the formation of HCN +N becomes more important. In order to clarify the discrepancy between the two studies we reevaluated the data from the previous study. From this reevaluation it can be concluded that the rate constant reported in the previous study for T >563 K are afflicted with an error resulting from a wrong calibration of the flow velocity in the reaction system and, consequently, should be deleted from future data evaluations. Thus, it can be summarized that even at 20 torr total pressure the addition channel (1b) leading to the formation of a HCN₂ adduct dominates the reaction.

Pressure Dependence

The observed pressure dependence of the CH + N_2 reaction which was investigated in the present study at four temperatures is consistent with the reaction mechanism proposed by Berman and Lin [5]. It should be pointed out that for all temperatures investigated the highest experimental pressures are far from the high pressure limit for this reaction. This is confirmed by the calculated half pressures listed in Table III where $k_{CH+N_2} = 1/2 k_{\infty}$.

At room temperature the values of the pressure limiting rate constants k_0 and k_{∞} from the present study are in good agreement, within the experimental accuracy, with data given by Wagal et al. [4] and Berman and Lin [5], see Table III.

For temperatures of 410, 561, and 750 K the pressure dependence of the CH + N₂ reaction was determined in the ranges 10-621, 20-613, and 20-618 torr, respectively. The data obtained at 750 K can be compared with a recent study of Medhurst et al. [8], however, the pressure dependencies were investigated in the present study for the first time at temperatures of 410 and 561 K. The result of a fit of the individual sets of rate constants to Troe's semiempirical equation [21-23] exhibits decreasing values both for k_0 and k_{∞} with increasing temperature, which is in accordance with the dominance of the addition pathway (1b) for temperatures < 1100 K. At 750 K, the k-values obtained in the present study are significantly larger than those reported by Medhurst et al. [8]. The difference between the two data sets increases with increasing temperature and amounts to more than a factor of five at 200 torr total pressure. In addition, at 750 K Medhurst et al. [8] observed no pressure dependence of $k_{\rm CH+N}$, for $p_{\rm tot} > 100$ torr, whereas even at the higher experimental pressure of the present study k_{CH+N_2} is far from the high pressure limit for this reaction.

An inter-comparison of the different pressure dependencies, Figure 4, shows that the pressure dependence at 750 K from the present study is consistent with the pressure dependencies obtained at 298, 410, and 561 K contrary to the findings from Medhurst et al. [8]. The reason for this discrepancy remains unclear.

In the present work, the temperature dependencies of the pressure limiting rate constants k_0 and k_{∞} were determined for the first time. The Arrhenius



Figure 6 Arrhenius plot of the bimolecular rate constant k_{∞} for the reaction CH + N₂ $\xrightarrow{[M]}$ HCN₂ vs. 1/T. The solid line is a weighted, linear least-squares fit to the data.

Pressure (Torr)	Temperature (K)	$k_{\rm CH+N_2}$ (cm ³ s ⁻¹)	$\frac{k_{abstr.}}{(cm^3 s^{-1})}$	Ratio k_{abstr}/k_{CH+N_2}
20 ± 1	752	6.0×10^{-15}	3.0×10^{-18}	5×10^{-4}
	672	8.7×10^{-15}	5.2×10^{-19}	6×10^{-5}
	572	16.5×10^{-15}	2.9×10^{-20}	2×10^{-7}
100 ± 1	1059	0.69×10^{-14}	2.1×10^{-16}	3×10^{-2}
	755	2.25×10^{-14}	3.2×10^{-18}	1×10^{-4}
	640	4.62×10^{-14}	2.3×10^{-19}	5×10^{-6}
620 ± 4	1016	1.7×10^{-14}	1.4×10^{-16}	8×10^{-3}
	914	2.9×10^{-14}	4.1×10^{-18}	1×10^{-3}
	742	9.3×10^{-14}	2.5×10^{-19}	3×10^{-5}

Table IV Contribution of the Abstraction Pathway $CH + N_2 \rightarrow HCN + N$ to the Overall Rate Constant k_{CH+N_2} ; Rate Constants k_{abstr} , were Extrapolated Using the Arrhenius Expression Given by Dean et al. [11]

parameters derived allow the calculation of bimolecular rate constants k_{CH+N_2} at any temperature and total pressure within the ranges 10-620 torr and 298-1100 K.

CONCLUSION

The reaction $CH(X^2\Pi) + N_2 \rightarrow products$ has been studied over wide temperature and pressure ranges by excimer laser photolysis (ELP)/laser-induced fluorescence (LIF). At all investigated total pressures, the Arrhenius plots exhibit a strong decrease of the bimolecular rate constant k_{CH+N_2} with increasing temperature, indicating that in the investigated temperature range the addition pathway leading to the formation of a HCN₂ adduct dominates the reaction.



Figure 7 Arrhenius plot of the bimolecular rate constant k_{CH+N_2} vs. 1/T at 100 torr total pressure. Data of this work (**•**) in comparison with literature data of Medhurst et al. [8] (O) and Bertman and Lin [5] (\Box). The solid line is a weighted, nonlinear least-squares fit to a three-parameter Arrhenius expression to the data of the present work.



Figure 8 Arrhenius plot of the bimolecular rate constant k_{CH+N_2} vs 1/T at 20 torr total pressure: (**II**) this work and (**II**) Becker et al. [6].

The pressure dependence of k_{CH+N_2} was investigated for several individual temperatures and the limiting rate constants k_0 and k_{∞} were calculated by Troe's semiempirical equation. From these results, the temperature dependencies of k_0 and k_{∞} were determined. By using the obtained data, bimolecular rate constants k_{CH+N_2} can be calculated at any temperature and total pressure within the investigated pressure and temperature ranges 10-620 torr and 298-1100 K, respectively.

However, experiments determining the pressure dependence of the $CH + N_2$ reaction up to several hundred bar at various temperatures and further calculations of the energy hypersurface would be very useful for a better understanding of this very important reaction, in particular, in order to clarify the importance of the datively bound HCN_2 complex in the overall reaction. Financial support by the Deutsche Forschungsgemeinschaft (DFG) and the Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen (MWF) is gratefully acknowledged.

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