

Rates of the reactions $\text{CN} + \text{H}_2\text{CO}$ and $\text{NCO} + \text{H}_2\text{CO}$ in the temperature range 294–769 K

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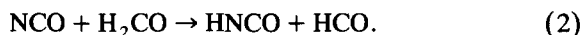
Abstract

The rate coefficients of the reactions: (1) $\text{CN} + \text{H}_2\text{CO} \rightarrow$ products, and (2) $\text{NCO} + \text{H}_2\text{CO} \rightarrow$ products in the temperature range 294–769 K have been determined by means of the laser photolysis-laser induced fluorescence technique. Our measurements show that reaction (1) is rapid: $k_1(294 \text{ K}) = (1.64 \pm 0.25) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; the Arrhenius relation was determined as $k_1 = (6.7 \pm 1.0) \times 10^{-11} \exp[(-412 \pm 20)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Reaction (2) is approximately a tenth as rapid as reaction (1) and the temperature dependence of k_2 does not conform to the Arrhenius form: $k_2 = 4.62 \times 10^{-17} T^{1.71} \exp(198/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Our values are in reasonable agreement with the only reported measurement of k_1 ; the rate coefficients for reaction (2) have not been previously reported.

1. Introduction

HCN is important in the ignition of nitramines and combustion of fuel-bound nitrogen [1–3]. CN and NCO radicals are two intermediates produced during oxidation of HCN. The NCO radical is also a key intermediate in a process RAPRENO_x (rapid reduction of nitric oxides), [4,5] to treat exhaust gases to decrease nitrogen oxides emitted from internal combustion engines. H_2CO is a product of thermal decomposition of composite propellant RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) [1]. We have investigated the kinetics of CN and NCO radicals with H_2CO to assess their importance in the combus-

tion system of nitrogen compounds, according to the following reactions:



Yu et al. [6] investigated the kinetics of reaction (1) using the laser photolysis-laser induced fluorescence technique. They observed non-Arrhenius behavior for reaction (1) between 297 and 673 K: $k_1 = 2.82 \times T^{2.72} \exp(718/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with $k_1 = (1.66 \pm 0.03) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K. Calculations for a loose transition structure yielded reasonable agreement with their experimental values. Tsang [7] estimated $k_1 = 7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ based on the rate coefficient of abstraction of an H atom by CN from propane [8].

No kinetic measurement of reaction (2) has been previously reported. Only the value $k_2 = 1 \times 10^{-11}$

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$\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with a negligible activation energy was estimated by Tsang [7].

In continuing the kinetic measurements on reactions of CN and NCO, needed to address the relevance of free radical reactions in the combustion chemistry of nitrogen compounds, we employed the laser photolysis (LP)-laser induced fluorescence (LIF) technique to investigate the kinetics of the title reactions in the temperature range of 294–769 K and with He at a pressure of 52–201 Torr.

2. Experimental section

The LP-LIF system employed in this work has been previously described [9]. The resistively heated reaction cell is a six-armed quartz flask with a volume of about 250 ml. Two pairs of baffled side arms fitted with Brewster windows are mounted mutually perpendicular and they are used to admit the dissociation and probing laser beams that cross at the center of the reactor. The arms are flushed with a small flow of He to avoid accumulation of photolytic products on the windows. The fluorescent signal was collected with a photomultiplier tube (Hamamatsu R955 or R212UH) through a set of lenses and an interference filter from the side window perpendicular to the laser beams. The LIF signal was amplified (Hamamatsu C1053-01,5 MHz) and averaged with a gated integrator (Stanford Research System, SR250). A microcomputer was used to store and to analyze the collected data.

CN radicals were produced by photolysis of ICN at 248 nm (KrF) or BrCN molecules at 193 nm (ArF) with an excimer laser (Lambda Physik LEXTRA 50). The concentration of CN radicals was monitored with a dye laser (Continuum ND60) at 387.63 nm pumped by a Nd-YAG laser (Continuum NY61) with a dye Exalite 389, which excited CN radicals from the $X^2\Sigma^+$ ($v''=0$) to the $B^2\Sigma^+$ ($v'=0$) state. The red-shifted ($v'=0 \rightarrow v''=1$) fluorescence was collected at a photomultiplier tube through an interference filter at 420 nm (35% transmission, fwhm = 10 nm) to minimize interference from scattered light.

NCO molecules were prepared via the rapid reaction (3a)



in which $k_3 = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [9], with the major product channel (3a) ($\sim 70\%$) [10,11]. The concentration of O_2 was at least $3.6 \times 10^{16} \text{ molecule cm}^{-3}$ so that in 10 μs reaction (3) went to $> 99.9\%$ completion. The $A(0,2^0,0)$ – $X(0,0^1,0)$ transition at 414.947 nm was chosen to monitor the concentration of NCO radicals because of its greater intensity and small lifetime (328 ns) [12]. The red-shifted fluorescence was collected through an interference filter at 439 nm (45% transmission, fwhm = 10 nm).

A delay/pulse generator (Stanford Research System, DG535) was used to set the delay between the photolysis and the probe lasers. The concentration of CN radicals at a fixed delay time was determined by sitting at a fixed delay for 30 to 100 laser shots to obtain a single fluorescence point in the decay curve. The reaction period was determined by the delay between the firing of the photolysis and the probe lasers. The lasers were generally operated at a repetition rate 10 Hz.

The precursors of NCO (ICN, BrCN, O_2), reactant H_2CO and buffer gas (He) were mixed in flexible tubing (length 30 cm) before entering the reactor and slowly flowed (flow velocity 7–20 cm s^{-1}) such that the reaction zone was replenished with a fresh gas mixture for each photolysis laser pulse.

The pressure of the system was measured with a MKS 122A Baratron gauge. Calibrated Tylan FM360 mass flowmeters were used to measure the flow rates of reactants and buffer gas. The temperature of the reaction was regulated within ± 1 K with an Omega CN9100A temperature controller and measured with a K-type thermocouple placed 5 mm above the detection region.

The concentrations of the reactants were calculated according to

$$[A] = 9.66 \times 10^{18} P F_A / F_T T \quad (\text{molecule cm}^{-3}), \quad (4)$$

in which P is the reaction pressure (in Torr), T is the reaction temperature (K), and F_A , F_T are the flow rates (in STP cm^3/s , STP = 273.15 K, 760 Torr) of reactant A and the total reaction mixture, respectively. The initial CN radical concentration produced by photolysis is estimated from

$$[\text{CN}]_0 = \sigma F [\text{XCN}], \quad (5)$$

in which $X = \text{I}$ or Br ; σ is the absorption cross section of ICN at 248 nm (a value $4 \times 10^{-19} \text{ cm}^2$ was used) [13], or BrCN at 193 nm ($3.3 \times 10^{-19} \text{ cm}^2$ was used) [14]; F is the fluence (photons cm^{-2}) of the dissociation laser.

Gaseous He (99.999%) and O_2 (99.97%) were used without further purification. ICN (Aldrich, 95%) was degassed before use. BrCN (Aldrich) was purified by freeze–pump–thaw cycles. H_2CO monomers were prepared by heating the polymer (paraformaldehyde) to 350 K, collected at 78 K and diluted in He to form a 0.5% mixture.

3. Results

All kinetic measurements were made under pseudo-first-order conditions with $[\text{H}_2\text{CO}]$ more than 200 times greater than $[\text{CN}]$ or $[\text{NCO}]$. The initial concentrations for CN and NCO were less than $4 \times 10^{11} \text{ molecules cm}^{-3}$, to avoid possible radical–radical reactions and to ensure pseudo-first-order conditions. The rate equation is expressed as

$$-d[\text{R}]/dt = k^1[\text{R}] = (k_d + k^{\text{II}}[\text{H}_2\text{CO}])([\text{R}]), \quad (6)$$

in which $\text{R} = \text{CN}$ or NCO , k^1 (in s^{-1}) is the first-order decay coefficient, k_d is the rate coefficient for radical loss due mainly to diffusion and k^{II} is the second-order reaction rate coefficient of interest.

CN + H_2CO reaction. The rate coefficient of reaction (1) was measured in the temperature range 294–769 K. Fig. 1 shows a typical set of CN decay plots whose slopes are used to determine the first-order rate coefficients k^1 . From these slopes we derived the second-order rate coefficients, k_1 . At 294 K, k_1 was measured for pressures in the range 52–201 Torr of He; we observed no pressure dependence of the rate coefficient (Fig. 2). We obtained a value $(1.64 \pm 0.04) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$; the uncertainty represents two standard deviations in the linear least-squares fit. Combining the estimated errors from the measured parameters (pressure, temperature, gas flow rates, slopes of decay plots) with possible systematic errors we estimated an overall uncertainty for k_1 about 15% at the 95% confidence level. Our value is in excellent agreement with that determined by Lin and co-workers [6]: $(1.66 \pm 0.04) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

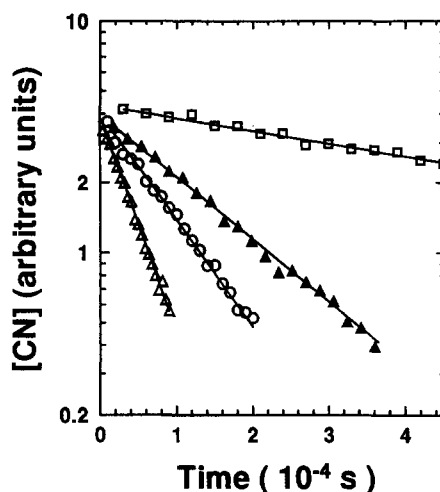


Fig. 1. Decay plots of CN at 769 K and 90 Torr with $[\text{H}_2\text{CO}]$ ($10^{14} \text{ molecules cm}^{-3}$) = 0, $k^1 = 1251 \text{ s}^{-1}$ (\square); 1.5, $k^1 = 6285 \text{ s}^{-1}$ (\blacktriangle); 2.5, $k^1 = 10185 \text{ s}^{-1}$ (\circ); 4.3, $k^1 = 17679 \text{ s}^{-1}$ (\triangle).

Plots of k^1 versus $[\text{H}_2\text{CO}]$ at various temperatures are shown in Fig. 3. All of the plots exhibited satisfactory linearity. The experimental conditions and k_1 measurements of this work are summarized in Table 1. Fig. 4 shows the Arrhenius plots of k_1 from our measurements. A linear fit gives $k_1 = (6.7 \pm 1.0) \times 10^{-11} \exp[-412 \pm 20/T] \text{ cm}^3 \text{ mole}^{-1}$

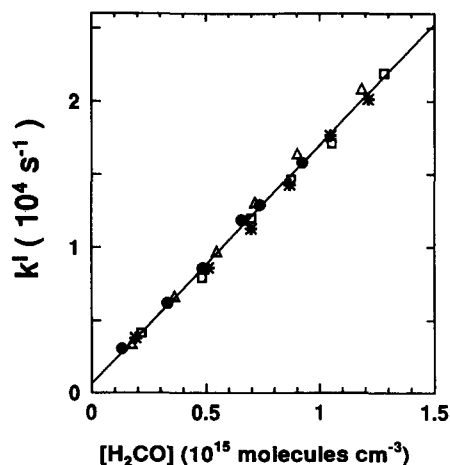


Fig. 2. Plots of pseudo-first-order decay rate of CN, k^1 , versus $[\text{H}_2\text{CO}]$ at 294 K and 52 Torr (\bullet); 100 Torr (Δ); 155 Torr (\square); 201 Torr ($*$).

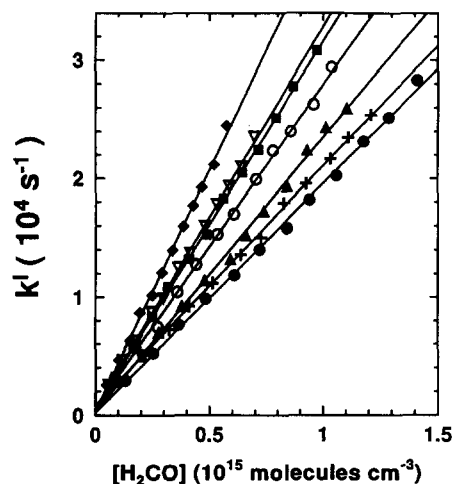


Fig. 3. Plots of pseudo-first-order decay rate of CN, k^1 , versus $[\text{H}_2\text{CO}]$ at 323 K (●); 357 K (+); 400 K (▲); 455 K (○); 526 K (■); 625 K (▽); 769 K (◇).

$\text{molecule}^{-1} \text{s}^{-1}$, the error limits are at the 95% confidence level.

NCO + H₂CO reaction. The rate coefficients of reaction (2) were measured over the temperature range of 294–769 K using CN + O₂ as a source of NCO. The temporal profile of $[\text{NCO}]$ (Fig. 5) shows a slow decay ($k^1 = 200\text{--}1200 \text{ s}^{-1}$, which varied with temperature) with no H₂CO present. The decay was probably due mainly to diffusion of NCO away from the detection zone. The rate of decay of NCO

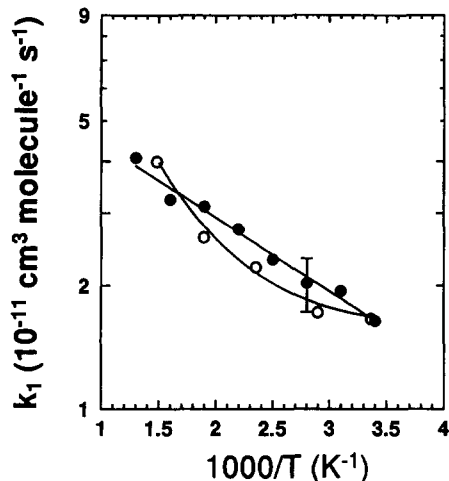


Fig. 4. Arrhenius plots of k_1 ; this work (●); Yu et al. (○).

Table 1
Summary of CN + H₂CO reaction data

T (K)	Pressure (Torr)	$[\text{H}_2\text{CO}] \times 10^{-14}$ (molecules cm^{-3})	$k_1 \times 10^{11}$ ^a ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
294	52–201	1.3–12.6	1.64 ± 0.04 ^b
323	100–105	1.3–14.1	1.94 ± 0.04
357	95–100	1.0–12.1	2.03 ± 0.02
400	95–100	0.9–11.0	2.32 ± 0.04
455	98–104	0.9–10.4	2.74 ± 0.02
526	92–98	0.9–9.7	3.11 ± 0.02
625	88–94	0.6–7.0	3.23 ± 0.02
769	89–94	0.5–5.7	4.08 ± 0.04

^a $k_1(T) = (6.7 \pm 1.0) \times 10^{-11} \exp[-(412 \pm 20)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^b The indicated error limits are 2σ .

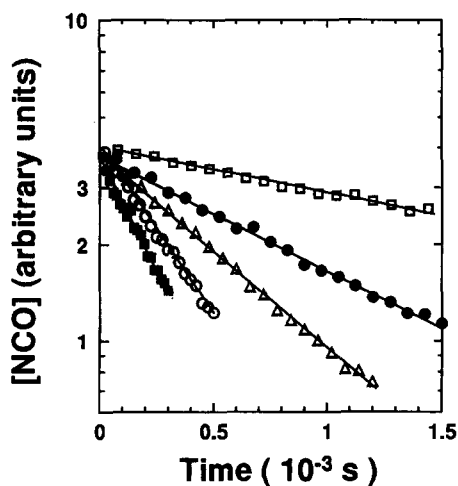


Fig. 5. Decay plots of NCO at 455 K with $[\text{H}_2\text{CO}]$ ($10^{15} \text{ molecules cm}^{-3}$) = 0, $k^1 = 320 \text{ s}^{-1}$ (□); 0.2, $k^1 = 828 \text{ s}^{-1}$ (●); 0.5, $k^1 = 1396 \text{ s}^{-1}$ (Δ); 0.9, $k^1 = 2408 \text{ s}^{-1}$ (○); 1.1, $k^1 = 3148 \text{ s}^{-1}$ (■).

Table 2
Summary of experimental conditions of the reaction NCO + H₂CO

T (K)	Pressure (Torr)	$[\text{H}_2\text{CO}] \times 10^{-14}$ (molecules cm^{-3})	$k_2 \times 10^{12}$ ^a ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
294	92–105	1.5–22.6	1.57 ± 0.03 ^b
323	90–100	1.3–20.4	1.63 ± 0.02
357	90–100	1.2–19.5	1.87 ± 0.03
400	90–100	0.9–15.1	2.19 ± 0.05
455	100–110	0.9–12.4	2.51 ± 0.08
526	90–100	1.1–15.7	3.06 ± 0.03
625	90–100	1.0–11.6	4.11 ± 0.06
769	90–100	0.8–8.9	5.16 ± 0.09

^a $k_2(T) = 4.62 \times 10^{-17} T^{1.71} \exp(198/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

^b The indicated error limits are 2σ .

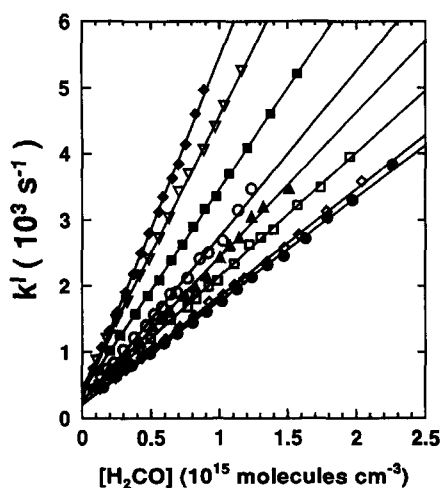


Fig. 6. Plots of pseudo-first-order decay rate of NCO, k^1 , versus $[\text{H}_2\text{CO}]$ at 294 K (●); 323 K (◇); 357 K (□); 400 K (▲); 455 K (○); 526 K (■); 625 K (▽); 769 K (◆).

increased significantly upon addition of H_2CO and the coefficients k^1 for the first-order decay rate were calculated from slopes of the semi-log plots. By fitting k^1 values versus $[\text{H}_2\text{CO}]$, as shown in Fig. 6, we obtained k_2 from the slope. Table 2 summarizes the experimental conditions and results; the error limits represent 2σ of our work on reaction (2). These measurements show that the temperature de-

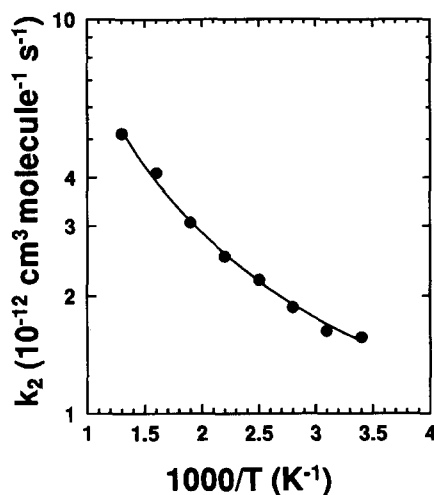


Fig. 7. Arrhenius plots of k_2 .

pendence of k_2 deviates from the Arrhenius form: $k_2 = 4.62 \times 10^{-17} T^{1.71} \exp(198/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, as plotted in Fig. 7.

4. Discussion

CN + H_2CO reaction. Yu et al. [6] recently published results of k_1 measurements (also shown in Fig. 4). They obtained a non-Arrhenius temperature dependence of k_1 between 297 and 673 K: $k_1 = 2.82 \times 10^{-19} T^{2.72} \exp(718/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. They also performed transition state theoretical calculations on reaction (1). The calculated and measured rate coefficients agreed reasonably well when a simple H-abstraction mechanism with loose transition state model was employed. Their measurements and this work are in good agreement at room temperature and at about 600 K but deviate approximately 10–14% in between, which is within the error limits of the measurements. However, the deviation is large when extrapolated to a flame temperature. Additional measurements at higher temperatures are needed before k_1 is applied to combustion models.

Yu et al. found that k_1 varied with the energy of the dissociation laser (~ 20 – 105 mJ/pulse): k_1 decreased with increasing laser energy. They attributed this dependence of k_1 to the photodissociation of H_2CO and determined k_1 using a small laser energy (≤ 30 mJ/pulse) to minimize this problem. In this work, the rate coefficients were determined at an energy 0.55–1.20 mJ of the dissociation laser (beam diameter of 5 mm) and we detected no dependence of k_1 on laser energy. The absorption cross section of formaldehyde at 248 nm is $\sim 1.0 \times 10^{-21} \text{ cm}^2 \text{ molecule}^{-1}$ (296 K) [15] and that at 193 nm is expected to be smaller than that at 248 nm. The loss of reactant due to photodissociation was negligible ($< 0.0002\%$) under our experimental conditions. In a data evaluation Tsang [7] estimated $k_1 = 7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ based on the measured rate coefficient of the similar H-atom abstraction reaction $\text{CN} + \text{C}_3\text{H}_8$ ($k = 3.3 \times 10^{-13} T^{0.56} \exp(649/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) [8]. His estimate is about four times as large as our result.

The reactions of CN with unsaturated hydrocarbons C_2H_2 and C_2H_4 are believed to proceed by a

mechanism of addition followed by H-atom elimination. The rate coefficients of those reactions feature nearly gas kinetic values ($2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature) and a slight negative temperature dependence ($E_a = -0.35 \text{ kcal mol}^{-1}$) [16]. However, CN reacts with H_2CO about 1/15 times as rapid as with C_2H_2 and C_2H_4 at room temperature and with an activation energy near 1 kcal mol^{-1} . Hence reaction (1) may occur via a simple H-abstraction mechanism analogous to the reaction $\text{CN} + \text{C}_2\text{H}_6$. The rate coefficients of these two reactions are similar in both magnitude and temperature dependence [17]. Formation of an adduct of CN added to the π system of formaldehyde is unlikely as the occupation of the anti-bonding $2b_1$ orbital by the unpaired electron of CN is energetically favored with a structure of the H–C–O angle near 90° that deviates significantly from its equilibrium structure. Lack of a pressure dependence of k_1 may further indicate a direct H-abstraction.

NCO + H₂CO reaction. The upward curvature on the Arrhenius plots of k_2 indicates that the activation energy of reaction (2) increases with increasing temperature. This phenomenon could be explained according to transition state theory with a loose transition structure [18]. The curved Arrhenius plots might also arise from quantum-mechanical tunneling.

We know of no previous investigation of the kinetics of reaction (2). Only an estimate $k_2 = 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was reported by Tsang [7], which is about ten times our value. The kinetics of reactions of NCO with hydrocarbons are investigated by several researchers [19–21]. Perry reported that the rate coefficient of the reaction $\text{NCO} + \text{C}_2\text{H}_4$ depended on pressure and decreased with increasing temperature [19]. Park and Hershberger observed a slight amount of HNCO produced from the reaction of NCO with C_2H_4 . An addition–elimination mechanism is evident for the reaction $\text{NCO} + \text{C}_2\text{H}_4$. In contrast, our measurements suggest that NCO radicals may not add to the double bond of H_2CO . Instead, reaction (2) occurs mainly via a simple H-abstraction path similar to reaction (1) with the same rationale.

We endeavored to evaluate and to eliminate all possible interfering reactions to ensure the accuracy of our kinetic measurements. The NCO source, reaction (3), also produces O, NO, and CO, with k_{3b}/k_{3a}

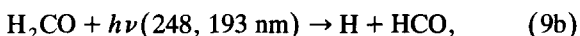
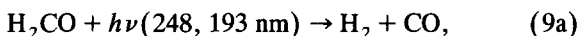
$= (0.3 - 0.4)$ [10,11]. Oxygen atoms and NO are known to react rapidly with NCO:



in which $k_7 = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [22], and $k_8 = 3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [7]. Under the experimental conditions $[\text{NCO}]_0 = 4 \times 10^{11} \text{ molecule cm}^{-3}$, the concentrations (in $10^{11} \text{ molecule cm}^{-3}$) of O, NO, and CO are approximately 4, 1, and 1, respectively. Hence a first-order loss of NCO $< 7 \text{ s}^{-1}$ would be due to reactions (7) and (8), which is negligible. Oxygen atoms produced in reaction (3a) react with H_2CO , $k(300 \text{ K}) = 1.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ [21]. Possible interference from this reaction was negligible under pseudo-first-order conditions, $[\text{H}_2\text{CO}] \gg [\text{O}] = [\text{NCO}]_0$.

NCO radicals produced from reaction (3) are known to be vibrationally excited [23]. A non-Boltzmann distribution of internal energy of the NCO reactant might introduce errors into the kinetic measurements because of slow relaxation to populate the monitored level and to the effects of internal energy on the reactivity of the radical toward H_2CO . No such error was expected in this work as all measurements were undertaken under pressures at least 90 Torr and relaxation periods greater than $10 \mu\text{s}$ to ensure a thermally equilibrated environment.

Photodissociation of formaldehyde produces reactive species,



that may react with CN and NCO radicals. At the largest concentration of H_2CO employed in this work, the concentrations of photodissociation products were less than $2 \times 10^{10} \text{ molecule cm}^{-3}$. Thus they cannot cause interference with the kinetic measurements.

In summary, we determined the rate coefficients of reactions of CN and NCO with H_2CO at 294–769 K using laser photolysis–laser induced fluorescence method. The measured values of k_1 are in reasonable agreement with the only published results. No kinetic measurement of k_2 is previously reported. Our investigation of the title reactions provide important information to improve understanding of the combustion chemistry of nitrogen compounds.

Acknowledgements

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