For reactions involving small moieties, incorporating a sinusoidal hindering potential improves the accuracy of the predicted rate coefficients over a wide range of conditions and provides more realistic descriptions of the transition states. A SHR can also be used to bypass the difficulties caused by hard-sphere steric interactions for systems such as CH_3OH and C_2H_6 . The model, however, becomes less valid with increasing temperature as the transition state becomes tighter. The results obtained compare favorably with those from more exact (and more complex) formulations, and from experiment, for cases where both moieties are comparatively small. However, for reactions involving a large moiety (e.g., a tert-butyl group), results are very sensitive to the assumed values for the van der Waals radii of the moiety (i.e., to the assumed interaction potential), and the method cannot be employed in such cases. The SHR model also fails to predict the slight negative temperature dependence of the recombination rate coefficient for two methyl radicals, although the actual predicted values are close to those observed experimentally; in order to predict such fine dependences, a more sophisticated model must be used.

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Absolute Rate Constants for the Reaction of CN with CH₄, C₂H₆, and C₃H₈ from 292 to 1500 K Using High-Temperature Photochemistry and Diode Laser Absorption

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By combining the laser-induced fluorescence detection technique with high-temperature reactor technology, absolute rate constants for the reaction of CN with CH_4 , C_2H_6 , and C_3H_8 have been measured as a function of temperature (292-1500 K) and pressure (5-60 Torr). CN radicals were generated by 193-nm excimer laser photolysis of dilute C_2N_2/Ar mixtures. Radical decays were monitored by laser-induced fluorescence from the $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ transition near 387 nm under pseudo-first-order conditions. Arrhenius plots of the rate constants show significant curvature. The temperature-dependent rate constants have been fit to modified Arrhenius expressions of the form $k = AT^{n} \exp(-E/T)$. This study represents the widest continuous temperature range over which rate constants for these reactions have been measured directly. The reaction kinetics and products of these reactions were also studied at 295 K by diode laser absorption. Rate constants obtained from product growth are in good agreement with the laser-induced fluorescence data. For these reactions at 295 K, HCN was found to be the dominant observable product.

Introduction

Reactions of the CN radical have practical significance because of the well-established role it plays in the conversion of fuel-bound nitrogen to NO during combustion.¹⁻³ For instance, reaction of CN with hydrocarbons present during the combustion of fossil fuels could generate HCN, which is an important precursor in the formation of NO. However, in spite of this importance, direct measurements of the rate constants for this species, particularly at high temperatures, are limited.

Studies of CN radical reactions with hydrocarbons performed prior to 1977 have been summarized by Baulch and co-workers.⁴ Most measurements were performed on the reaction of CN with CH₄. Higher hydrocarbons have received less attention. Rate constants for the reactions of CN with hydrocarbons beyond propane have not been reported. The methane data were obtained over narrow temperature ranges, from estimates, modeling complex processes, rate constant ratios, and theoretical calculations. Recently, several researchers have used the pulsed-photolysis laser-induced fluorescence (LIF) technique to obtain absolute rate constants for CN reactions at room temperature⁵⁻⁸ and as a function of temperature.⁵ These studies produced CN from a variety of precursors at several photolysis wavelengths, and data

The older studies were performed over relatively narrow temperature ranges so that accurate Arrhenius parameters could not be determined. The most recent results are in good agreement at room temperature. Our data represent the widest continuous temperature range over which this reaction has been studied by a single direct method.

The rate constants obtained from the high-temperature photochemistry study suggested that two different mechanisms might

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have been obtained by observing fluorescence from both the $A^2\Pi$ and the $B^2\Sigma^+$ states of CN. Other researchers have studied CN reactions using absorption spectroscopy to monitor CN decay.9-11

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be occurring over the temperature range studied. To investigate this possibility, diode-laser absorption experiments were used to monitor the products in real time. Results indicate that HCN is the dominant observable reaction product at room temperature. These experiments were the first to use direct methods to monitor the products of the reactions of CN with hydrocarbons.

Experimental Section

The high-temperature photochemistry (HTP) experimental apparatus has been described in detail previously.¹² CN radicals are produced by pulsed laser photolysis of cyanogen (C_2N_2) using 193-nm radiation. The CN radical concentration is probed by laser excitation of either the $R_{0-0}(9)$ line near 386.9 nm or the $P_{0-0}(7)$ line near 388.0 nm of the $B^2\Sigma^+ \leftarrow X^2\Sigma^+$ system and by monitoring the resulting fluorescence near 420 nm from the (0,1) band. The photolysis laser is a Lambda Physik Model EMG 101 excimer laser (10 Hz, 180 mJ/pulse at 193 nm, 10 ns pulse length), while the LIF excitation source is a Lambda Physik Model FL2002 dye laser, using BBQ dye, pumped by a Lambda Physik Model EMG 101E excimer laser.

The pump and probe lasers counterpropagate collinearly through a high-temperature photochemistry reactor whose design is similar to that of Felder et al.¹³ The fluorescence emission from the (0,1) band is collected with f/4 collection efficiency at right angles to the laser beams and focused onto an uncooled RCA 31034 photomultiplier tube (PMT). The photomultiplier output is amplified by a PAR Model 115 wide-band preamp, averaged by a PAR Model 162 boxcar integrator, and digitized and analyzed by a laboratory microcomputer. The data are normalized by both photolysis and excitation laser energies.

The delay time between the firing of the photolysis and probe lasers is controlled by the computer through a digital delay generator and is scanned from 5 μ s to 10 ms to obtain kinetic data for the radical decay. Data collection is initiated following a fixed delay time after the photolysis pulse. This delay was varied 5 to 50 μ s for experiments performed at room temperature in order to check for effects due to rotational and vibrational relaxation of the CN as well as to avoid unwanted scatter from the photolysis laser. Within experimental error, rate constants are independent of initial delay time. At all temperatures above 292 K, the initial delay time was fixed at 5 μ s to avoid interference by prompt fluorescence from photolysis products. The signal background is obtained 10 μ s before the firing of the photolysis laser.

Temperatures within the HTP reactor are measured by using an unshielded thermocouple rake and a shielded thermocouple mounted parallel to the central axis of the reaction tube. The temperature profiles within this system were determined by using the approach of Fontijn and Felder¹⁴ to estimate errors due to radiative heat transfer in the measured gas temperatures using our shielded and unshielded thermocouple data. These temperature measurements are in good agreement with temperatures derived from CN rotational distributions. These measurements as well as a description of the thermocouple corrections have been detailed previously.¹²

All reagents are used without further purification. Cyanogen (98.5% liquid phase) is obtained from Matheson. Argon (UHP grade, 99.999%), methane (Scientific Grade, 99.9995%), ethane (CP grade, 99.0%), and propane (Instrument Grade, 99.5%) are obtained from MG Scientific. Metered flows of cyanogen, hydrocarbons, and argon are combined and flowed through the cell at total flow rates ranging from 0.5 to 2 standard L/min. All component gases in the experiment are combined at a distance from the cell that ensures uniform mixing. The cyanogen, ethane, and propane are prepared as a 0.1-1.0% mix in argon. Methane is flowed directly from the tank except at the highest temperatures, where it is prepared as a 10% mix in argon. Typical reactant pressures are 1-4 mTorr of C_2N_2 , 0-10 Torr of CH_4 , 0-30 of

mTorr ethane and propane, and 5-60 Torr of argon.

The diode-laser absorption (DLA) system, described in detail previously,⁶ will be summarized here. CN is produced via photodissociation of C_2N_2 using an ArF excimer laser (Lambda Physik Model 101 MSC, 13 Hz, 30 mJ/pulse at 193 nm, 10 ns pulse length) in a 2 m \times 5 cm ID cylindrical Pyrex tube with BaF₂ windows. CN is probed with a diode laser (Laser Analytics, Model LS-3) whose output makes a single pass through the reaction cell. A cryogenically cooled tunable lead-salt laser is tuned to an absorption line of the molecule of interest. A Czerny-Turner monochromator and liquid nitrogen cooled HgCdTe detector select and monitor the absorption signal. The time-resolved transient absorption of the species of interest is acquired by using a digital oscilloscope and transferred to a microcomputer for storage and analysis. All DLA experiments are performed at 10 Torr of total pressure using nitrogen as a buffer gas. HCN is observed to both grow and decay on the time scale of these experiments. The temporal profile of all species is obtained by averaging 500 separate transient absorption experiments. The HCN growth signal can be fit by a single exponential extending 2-4 lifetimes. The HCN molecule is monitored by using the $(0,0,1) \leftarrow (0,0,0)$ P(10) transition of the ν_3 band at 3284.13 cm^{-1.15} The CH₃CN molecule is monitored on the PQ_3 transition at 1026.03 cm⁻¹ and the PQ_0 transition at 1042.13 cm^{-1.16} The HNC molecule is searched by probing the $(0,0,1) \leftarrow (0,0,0)$ P(8) transition of the ν_3 band at 1999.05 cm^{-1 17} although several other rotational transitions were also probed. Arsine (AsH₃) was used as a reference gas to confirm spectral position. The rovibrational lines have been assigned by Olson et al.¹⁸ to $\pm 1 \times 10^{-3}$ cm⁻¹. Various transitions from H₂O, CO, and CO_2^{19} were also used where appropriate.

Gas purities on the DLA experiments were slightly below those of the HTP study. All reagents were used without further purification. Cyanogen (98.5% liquid phase) was obtained from Matheson. Methane (99.97%) and ethane (>99.0%) were obtained from Liquid Carbonic, while nitrogen (99.998%) was obtained from Air Products. Metered flows of cyanogen, hydrocarbons, and nitrogen were combined and flowed through the cell at total flow rates ranging from 0.5 to 2 standard L/min. All component gases in the experiment were combined at a distance from the cell ensuring uniform mixing. The cyanogen and ethane were prepared as a 0.1-1.0% mix in nitrogen. Methane was flowed directly from the tank. Typical reactant pressures were 50-300 mTorr of C_2N_2 , 0-2 Torr of CH₄, 0-1 Torr of ethane, and approximately 10 Torr of nitrogen.

Results

The CN radical $(X^2\Sigma^+)$ is produced by photolyzing C_2N_2 using 193-nm radiation. To minimize the removal of CN by all processes except reactions with the alkanes, all experiments to measure rate constants are performed under pseudo-first-order conditions, i.e., for the case of CN reaction with methane, $[CH_4] \gg [CN]$, $[C_2N_2]$, and [HCN]. In the absence of any reactant, CN decays via self-reaction, reaction with C_2N_2 , and diffusion. When reactants are present in sufficient concentrations, the CN disappearance is dominated by the bimolecular reaction of interest,

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Figure 1. Decay of CN LIF signal at 1488 K in the presence of CH₄. $P(C_2N_2) = 5 \text{ mTorr}$, $P(CH_4) = 145 \text{ mTorr}$, P(total) = 30 Torr. Each point represents one laser shot. The solid line is the result of an exponential fit to the data.



Figure 2. Plot of the observed CN radical decay constant versus CH₄ pressure at 1488 K for the reaction of CN + CH₄. Argon was used as a buffer gas at 15 Torr of total pressure. The slope represents the second-order rate constant for the reaction of CN + CH₄ at 1488 K. The intercept represents the rate of all other first-order CN removal processes. All uncertainties represent $\pm 1\sigma$.

which can be fit by a single exponential extending typically over 2-4 lifetimes. It can be represented by the expression

$$-d[CN]/dt = k_1[CN][CH_4] + k_d[CN]$$

where k_d [CN] includes diffusion out of the region sampled by the probe laser beam and removal created by the flow conditions of these experiments. In the HTP experiments, bimolecular rate coefficients were determined from the slopes of these first-order CN decays versus reactant concentration for the reactions of CN with methane, ethane, and propane over a range of temperatures (292-1488 K) and total pressures (5-80 Torr) with Ar as a buffer gas. These rate coefficients together with the experimental conditions are listed in Table I. CN disappearance rates are independent of pressure, flow velocity, and probe distance for all hydrocarbons studied at temperatures below 1300 K. At higher temperatures, pyrolysis of ethane and propane is possible, as will be discussed later.

Figure 1 shows the real-time decay of CN reacting with CH_4 following excimer laser generation of the radical population. The curve consists of 501 points plus 20 prephotolysis baseline points. This decay was observed at our highest temperature, 1488 K, where measurements are most difficult and represents our least precise data. All other decays contain considerably less noise. The pseudo-first-order decay constant is calculated by fitting the single-exponential decay intensity as shown in Figure 1. By repeating this procedure at various alkane pressures, we calculate



Figure 3. Arrhenius plot for the reaction of $CN + CH_4$ from 292 to 1500 K. Fit is to the form $k = AT^n \exp(-E/T)$. All uncertainties represent $\pm 2\sigma$.



Figure 4. Arrhenius plot for the reaction of $CN + C_2H_6$ from 292 to 1500 K. Fit is to the form $k = AT^n \exp(-E/T)$. All uncertainties represent $\pm 2\sigma$. Also shown (\diamond) are the recent CN + ethane data of Hess et al.⁵



1000/T(K)

Figure 5. Arrhenius plot for the reaction of $CN + C_3H_8$ from 292 to 1500 K. Fit is to the form $k = AT^* \exp(-E/T)$. All uncertainties represent $\pm 2\sigma$. Also shown (\blacktriangle) are the recent CN + propane data of Hess et al.⁵

the second-order rate constant k_1 from the slope of plots of the first-order rate constants versus alkane partial pressure. A representative second-order plot is shown in Figure 2. In the vast majority of cases, the intercept is at least 1 order of magnitude slower than the fastest measured pseudo-first-order decay constant. These measurements were repeated at temperatures ranging from 292 to 1500 K. These results are shown in Figures 3-5 for reactions of CN with CH₄, C₂H₆, and C₃H₈, respectively.

In the DLA experiments, bimolecular rate coefficients were obtained for the reaction of CN by observing product formation.

TABLE I: Rate Coefficients for the Reactions of CN with Hydrocarbons^c

reactant	<i>т</i> . к	<i>P</i> , Torr	$k \times 10^{12}$, cm ³ /(molecule s)	v, cm/s	l, cm	E(J), mJ	$[reactant]_{max} \times 10^{-16},$ molecules/cm ³
CH.	292	20	0.812 ± 0.058	57.0	14	20	10.9
0114	292	20	0.751 ± 0.045	63.0	15	20	10.9
	386	10	1.37 ± 0.03	132.0	14	15	5.1
	417	10	1.94 ± 0.14	182.0	15	10	2.3ª
	465	20	2.12 ± 0.09	51.0	4	15	8.2
	526	10	2.73 ± 0.16	123.0	15	10	0.56ª
	593	20	2.89 ± 0.14	66.0	4	15	1.4
	614	30	3.56 ± 0.35	47.0	15	10	6.4 ^a
	714	30	5.84 ± 0.20	56.0	15	10	0.27*
	735	20	4.15 ± 0.30	94.0	4	15	1.0
	776	20	5.24 ± 0.28	100.0	14	15	1.0
	833	30	6.13 ± 0.52	65.0	14	10	0.35ª
	833	30	7.51 ± 0.22	65.0	14	10	0.15ª
	872	10	7.09 ± 0.42	223.0	14	15	0.45
	888	30	10.7 ± 0.4	65.0	15	10	0.16 ^a
	912	30	9.41 ± 0.38	105.0	15	20	0.394
	927	30	12.0 ± 1.0	73.0	7	10	0.13ª
	1020	30	12.8 ± 0.8	79.0	14	10	0.13ª
	1139	20	17.0 ± 1.2	130.0	9	15	0.41
	1152	30	20.4 ± 1.5	89.0	15	10	0.084
	1212	30	19.8 ± 0.4	128.0	15	20	0.24ª
	1322	15	21.5 ± 0.8	227.0	15	20	0.13ª
	1322	60	19.8 ± 1.1	90.0	15	20	0.22ª
	1488	30	28.7 ± 1.1	159.0	15	20	2.0ª
	1488	10	37.8 ± 2.6	477.0	15	20	0.13ª
	295 ⁶	10	0.46 ± 0.03			10	6.2
C ₂ H ₆	292	5	23.9 ± 1.7	126.0	15	20	0.07
	292	50	22.7 ± 1.6	265.0	15	20	0.30
	293	20	22.7 ± 1.4	38.0	14	15	0.99
	386	10	35.0 ± 1.6	132.0	14	15	2.3
	465	20	31.0 ± 2.2	51.0	4	15	1.2
	568	20	32.8 ± 1.3	66.0	4	15	1.2
	698	20	42.1 ± 2.1	97.0	4	15	1.0
	816	20	43.8 ± 3.2	100.0	14	15	1.0
	864	10	42.2 ± 2.8	223.0	14	15	1.0
	1020	30	101.0 ± 4.0	79.0	14	10	0.48ª
	1139	30	102.0 ± 2.0	66.0	6	15	0.14
	1409	30	78.5 ± 3.0	130.0	7	15	0.28ª
C ₃ H ₈	293	20	68.0 ± 5.2	38.0	15	15	0.33
	386	10	76.6 ± 7.5	123.0	15	15	0.10
	465	20	76.2 ± 4.9	51.0	4	15	0.08
	568	20	79.7 ± 1.7	65.0	4	15	0.07
	698	20	78.9 ± 5.9	97.0	4	15	0.04
	816	20	83.5 ± 5.6	100.0	14	15	0.05
	872	10	109.0 ± 5.0	223.0	14	15	0.02
	1020	30	135.0 ± 6.0	79.0	14	15	0.03ª
	1266	15	145.0 ± 3.0	199.0	15	15	0.02ª
	1266	15	141.0 ± 3.0	199.0	5	15	0.02ª
	1266	15	139.0 ± 6.0	199.0	2	15	0.02ª
	1266	60	137.0 ± 4.0	50.0	5	10	0.02ª
	1409	30	105.0 ± 4.0	130.0	7	15	0.02ª

^a Fluorescence excited using the $P_{0-0}(7)$ line. ^b Data acquired by DLA monitoring of HCN growth with N₂ as buffer gas. ^c Listed uncertainties represent $\pm 1\sigma$. Fluorescence excited using the $R_{0-0}(9)$ line of CN unless noted.

All data were acquired at 295 K and 10 Torr of total pressure under pseudo-first-order conditions. The CN radical $(X^2\Sigma^+)$ was produced by photolyzing C_2N_2 using 193-nm radiation. The growth of HCN produced by reaction of CN with CH₄ was monitored to obtain the rate coefficient, presented in Table I. Growth and decay plots of HCN similar to those observed in this experiment as well as a detailed analysis have been published previously.9 Since the HCN decay is slow compared to the rise time, the decay curve is stripped from the signal to obtain a growth plot. This produces a product growth plot analogous to the decay curve shown in Figure 1, from which the pseudo-first-order rate constant can be determined. Data obtained for the reaction of CN with methane are plotted in Figure 6. The rate coefficient for the reaction of CN with methane obtained by measuring HCN growth is $(4.6 \pm 0.6) \times 10^{-13} \text{ cm}^3/\text{s}$. The uncertainty is statistical only and represents $\pm 2\sigma$. Although this number is lower than the CN disappearance rate, it is somewhat less accurate since the rise time cannot be measured over as many exponential lifetimes as can the decay. In addition, there are other experimental difficulties due to excimer laser scattered light and rf pickup that affect the accuracy.

Other possible exothermic reaction products include HNC and CH₃CN as shown in Table II. All attempts to observe these products at room temperature using DLA in time-resolved measurements failed. No attempt was made to observe CH₃NC, since it is an endothermic product of the reaction with CH₄ at room temperature. Our data indicate that under equivalent conditions, the signal for CH₃CN is approximately 2 orders of magnitude weaker than the HCN signal. This lack of sensitivity could obscure the detection of CH₃CN in real time. The relative line strength of HNC to HCN was not determined. In an attempt to detect both HNC and CH₃CN, a mixture of cyanogen (3.5 Torr) and methane (14.8 Torr) or ethane (17.5 Torr) was photolyzed under static conditions, using 30 mJ/pulse of 193-nm radiation at a repetition rate of 10 Hz. These conditions are quite different from those used in the flow studies in that a much higher concentration of C_2N_2 is used in order to improve the possibility of detecting HNC or CH₃CN. Calibration was performed by



Figure 6. Second-order plot of the reaction of CN with CH₄ measured by observing via diode laser absorption (DLA) the growth of HCN at 295 K. All uncertainties represent $\pm 2\sigma$.

TABLE II: Possible Products and Exothermicities for the Reaction of CN with Hydrocarbons^a

reaction	$\Delta H(300)$, kcal/mol
$CN + CH_4 \rightarrow CH_3 + HCN$	-16.5
$CN + CH_4 \rightarrow CH_3CN + H$	-12.0
$CN + CH_4 \rightarrow CH_3 + HNC$	-6.0
$CN + CH_4 \rightarrow CH_3NC + H$	5.0
$CN + C_2H_6 \rightarrow CH_3CN + CH_3$	-27.5
$CN + C_2H_6 \rightarrow C_2H_5 + HCN$	-22.0
$CN + C_2H_6 \rightarrow C_2H_5CN + H$	-14.0
$CN + C_2H_6 \rightarrow C_2H_5 + HNC$	-12.0
$CN + C_2H_6 \rightarrow CH_3NC + CH_3$	-11.0
$CN + C_2H_6 \rightarrow C_2H_5NC + H$	2.0
$CN + C_3H_8 \rightarrow C_2H_5 + CH_3CN$	-30.0
$CN + C_3H_8 \rightarrow C_2H_5CN + CH_3$	-27.0
$CN + C_3H_8 \rightarrow i \cdot C_3H_7 + HCN$	-26.3
$CN + C_3H_8 \rightarrow n - C_3H_7 + HCN$	-22.9
$CN + C_3H_8 \rightarrow i - C_3H_7CN + H$	-18.5
$CN + C_3H_B \rightarrow i - C_3H_7 + HNC$	-16.0
$CN + C_3H_8 \rightarrow n - C_3H_7CN + H$	-15.0
$CN + C_3H_8 \rightarrow n - C_3H_7 + HNC$	-13.0
$CN + C_3H_8 \rightarrow C_2H_5NC + CH_3$	-11.0
$CN + C_3H_8 \rightarrow C_2H_5 + CH_3NC$	-14.0
$CN + C_3H_8 \rightarrow i - C_3H_7NC + H$	-1.0
$CN + C_3H_8 \rightarrow n - C_3H_7NC + H$	2.0

^e Where available, heats of formation taken from Benson,^{20s} Evans et al.,²⁰⁶ or Maki and Sams.¹⁷⁶ Otherwise, data calculated by using group additivity.20a

comparing the observed signals following photolysis to known product concentrations. After 18 excimer laser pulses, HCN absorptions were observed corresponding to 0.9 mTorr of HCN with methane and 1.0 mTorr of HCN with ethane. The HCN yield increased linearly with the number of laser shots. Averaging several experiments, this implies 0.05 ± 0.01 mTorr of HCN per excimer laser pulse in the presence of methane and 0.055 ± 0.01 mTorr of HCN per pulse in the presence of ethane. After 6000 pulses under similar reactant conditions, the total yields of CH₃CN corresponded to <1.5 mTorr with methane reactant gas and <0.5 mTorr with ethane, corresponding to a yield per laser pulse of $<2.5 \times 10^{-4}$ mTorr in the presence of methane and $<8 \times 10^{-5}$ mTorr in the presence of ethane. The room temperature branching ratios (HCN/CH₃CN) are >200:1 for reaction with methane and >500:1 for ethane. No HNC was observed after 12000 excimer laser pulses. Ethylene was observed in the ethane experiments, most likely from the disproportionation of ethyl radicals. Since HCN and CH₃CN are essentially unaffected by 193-nm radiation,²¹ they are not influenced by the long irradiation times of these experiments. To test their sensitivity to radical removal, approximately 1.5 mTorr of HCN and 120 mTorr of CH₃CN were added separately to 3 Torr of C_2N_2 and 9 Torr of CH₄ or 16.5 Torr of C_2H_6 . Following 6000 excimer laser pulses at two different energy levels (30 mJ/pulse and 50 mJ/pulse), neither species was found to be formed or removed to any significant extent.

Following this experiment, a 10-mL gas sample was withdrawn and injected into a Fourier-transform mass spectrometer. The ionization potential was systematically varied from 15 to 70 eV in an attempt to maximize signals from the parent ions. Under all conditions, no acetonitrile was observed (detection limit approximately 1% of the HCN concentration). The only measurable product was HCN.

Discussion

There are several potential photochemical sources of CN, including NCNO, XCN (where X = F, Cl, Br, I), and C₂N₂. C₂N₂ was chosen as the photolytic precursor because it is a clean source of CN and does not undergo an appreciable degree of thermolysis at the high temperatures used in this study. However, a potential problem with this precursor is the photolytic production of vibrationally and rotationally excited CN as has been observed at room temperature.^{22,23} Rotational equilibration to 300 K occurs in less than 5 μ s with 6 Torr of argon,^{7,24} while vibrational relaxation is slower. If vibrational quenching occurs on a time scale comparable to the observed decay time of CN(v''=0), the observed rate coefficients could be in error. The problem of vibrationally excited CN interfering with kinetic measurements has been discussed previously.¹² A modeling study has shown that CN(v''=1)quenching effects are negligible under these experimental conditions. Under the experimental conditions used in this study, if quenching were important, the pseudo-first-order decay plots (Figure 1) would not be single exponential. This effect was not observed, indicating that quenching effects created by the relaxation of vibrationally excited CN did not measurably influence our results.

All possible reactions of CN with the hydrocarbons are listed in Table II along with their exothermicities at 300 K. Although there are several secondary exothermic reactions that CN can undergo, there are no known exothermic secondary chemical reactions that can produce CN. Furthermore, all decays measured were single exponentials. If secondary reactions were producing significant amounts of CN, we would expect to see biexponential behavior.

The reactions of CN with hydrocarbons exhibit nonlinear Arrhenius behavior as shown in Figures 3-5. Therefore, it is important to discuss all possible experimental factors that might contribute to these results. The first of these factors to be considered is the possible hydrocarbon photodissociation at 193 nm. According to Calvert and Pitts,²⁵ absorption above 160 nm is negligible for methane, ethane, and propane. Second, at the high temperatures used in this study, thermal decomposition could occur. However, other workers have shown that, at the temperatures in this study, C₂N₂,²⁶ CN, and HCN^{27,28} are thermally stable. Both methane and ethane decomposition kinetics are in the low-pressure limit in this study.²⁹ Under the conditions used in our experiments, results suggest²⁹ that methane at 1500 K and 30 Torr of argon decomposes less than 0.1% under the minimum flow rates studied and ethane at 1100 K decomposes less than 2% under similar conditions. The ethane results are supported by

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Mahmud et al.³⁰ who used a similar apparatus and observed no decomposition of ethane at temperatures below 1250 K. For propane, the high-pressure rate coefficient for propane decomposition has been measured²⁹ by using more than 600 Torr of argon as a buffer gas. Using these results, we calculate that a significant fraction of the propane would decompose at 1260 K with a 10-ms residence time. No information is available on the pyrolysis of propane at low pressures. Measurements performed in our apparatus to assess the decomposition of propane at low pressures are independent of probe distance and flow velocity at 1266 K for a 10-fold change in residence time. If significant pyrolysis occurred, the probe study would exhibit a trend in rate constants as a function of probe distance. None was observed. These results indicate that significant pyrolysis of these compounds does not occur under the conditions of these experiments at temperatures less than or equal to 1270 K.

At temperatures above 1270 K, both Arrhenius plots for ethane and propane show a marked decrease in rate coefficients. The pyrolysis of both ethane and propane most likely becomes significant at these temperatures. We calculate from data presented by Warnatz²⁹ that all of the ethane decomposes in 54 ms at 1500 K and 30 Torr of argon. Although radical or unsaturated decomposition products might be expected to react with CN faster than the alkanes, they also would be expected to react with other decomposition products, the alkanes, and C_2N_2 . The removal of reactants by pyrolysis most likely accounts for the downward trend in rate coefficients for both ethane and propane at these temperatures.

CN + Methane. The temperature dependence of the reaction of CN with methane has been measured over the temperature range 292-1488 K. The Arrhenius plot of the measured rate coefficients is shown in Figure 3. The observed curvature of the Arrhenius plot can be explained either by the presence of multiple reaction channels or by a modified, three-parameter Arrhenius expression. Table II lists four possible reaction channels for CN + CH₄. Of these channels, the methyl isocyanide (CH₃NC) reaction is endothermic, making it unlikely to be an important product. Other possible products are HNC, HCN, and CH₃CN. HCN is the thermodynamically favored product. A search for the products was performed at room temperature, as discussed previously. HCN was found to be the dominant product, while CH₃CN was only observed after multiple laser shots on a static gas. Consequently, a single mechanism seems most likely.

A three-parameter modified Arrhenius expression of the form $AT^n \exp(-E/T)$ is characteristic of a reaction that can be described by transition-state theory where the formation of the transition state is a temperature-dependent process. This phenomenon is especially noticeable in those reactions whose effective activation energy is small. Parameters for the modified Arrhenius expression were determined from a weighted least-squares fit of the data to the linearized expression

$$\log (k) = \log (A) + n \log (T) - E/2.303T$$

producing

$$k = [(1 \pm 2) \times 10^{-19}] T^{(2.64 \pm 0.24)} \exp[(+220 \pm 150)/T] \text{ cm}^3/(\text{molecule s})$$

The quoted uncertainties reflect $\pm 1\sigma$ standard deviations derived from the fit. The large uncertainties in the estimated parameters are due to the high degree of coupling between the fit parameters, indicating that the individual parameters are not entirely independent of one another. However, these parameters can reproduce the experimental data with a standard deviation of about $\pm 15\%$.

CN + Ethane. The temperature dependence of the reaction of CN with ethane has been measured over the temperature range 292-1400 K. The Arrhenius plot of the rate coefficient shows considerable curvature (Figure 4). As discussed previously, py-

TABLE III: Room Temperature Rate Coefficients for the Reaction of CN with Hydrocarbons^a

		$k \times 10^{13}$,		
reactant	<i>T</i> , K	cm ³ /(molecule s)	technique ^b	ref
CH₄	291	8.12 ± 1.16	LIF	this work
•	292	7.55 🛳 0.90	LIF	this work
	298	7.8 🏚 0.8	DLA	9
	300	14.4 ± 0.12	LIF	8
	294	$11.3 \pm 0.6^{\circ}$	LIF	6
	293	5 ± 3	KAS	10
	300	7.4 🏚 0.2	KAS	11
	300	5.6 🛳 0.3	LIF	7
		$k \times 10^{11}$,		
reactant	<i>Т</i> , К	cm ³ /(molecule s)	technique ^b	ref
C2H6	292	2.39 ± 0.34	LIF	this work
2 0	292	2.27 ± 0.32	LIF	this work
	293	2.27 ± 0.28	LIF	this work
	294	2.9 ± 0.10	LIF	6
	300	2.41 ± 0.17	KAS	11
	294	2.84 🛳 0.14	LIF	5
C_2D_6	294	1.36 ± 0.07	LIF	5
C ₃ H ₈	293	6.80 ± 1.0	LIF	this work
	294	8.34 单 0.52	LIF	5
	300	5.3 🏚 0.8	KAS	11
C_3D_8	294	5.32 ± 0.38	LIF	5

^aListed uncertainties represent $\pm 2\sigma$. ^bLIF = laser-induced fluorescence; KAS = kinetic absorption spectroscopy; DLA = diode laser absorption. ^cData based on A \leftarrow X probing.

rolysis of ethane becomes significant at temperatures greater than 1140 K. The observed decline in the rate constant at 1409 K is most likely due to pyrolysis.

We have fit the data, excluding the point at 1409 K, to a three-parameter modified Arrhenius equation $AT^n \exp(-E/T)$ in a manner similar to that for the methane data and obtained

$$k = [(2 \pm 7) \times 10^{-19}] T^{(2.77 \pm 0.59)} \exp[(+900 \pm 300)/T] \text{ cm}^3/(\text{molecule s})$$

The uncertainties are $\pm 1\sigma$ derived from the fit. As with methane, the large uncertainties are due to the correlation among the fit parameters. This parameter set adequately reproduces the experimental data with a standard deviation of approximately $\pm 20\%$. A four-parameter fit was also performed. Although it appears to describe the data better, there are insufficient high temperature data to justify the addition of a second exponential term in the fit. In addition, the preexponential factor of the first term is 2 orders of magnitude faster than gas kinetic and the fit is not sensitive to its value. Consequently, it is of little help in suggesting a second, high-temperature mechanism for this reaction.

The data in Table II indicate that several reactions are possible on thermodynamic grounds. Also, formation of HCN is no longer the most exothermic channel at room temperature. However, a product search revealed HCN as the major products with traces of CH₃CN and C₂H₆. No HNC was observed and no attempt was made to detect C₂H₅CN.

Recent experiments of Hess, Durant, and Tully⁵ for the reaction of CN with ethane over the temperature range 292–725 K obtained results similar to ours. However, their rate coefficients were uniformly 15–20% larger than those measured in our study, although they were within the combined 2σ uncertainties. The higher temperature experiments reported here, however, suggest considerably greater curvature in the Arrhenius plot than would be extrapolated from the data of Hess et al.⁵ Theoretical calculations as well as additional high-temperature experiments would be helpful in identifying the processes contributing to this curvature.

CN + Propane. The temperature dependence of the reaction of CN with propane has been measured over the temperature range 292–1409 K. Figure 5 shows the Arrhenius plot of these data. As discussed previously, pyrolysis of propane becomes significant at temperatures higher than 1270 K, making it the most likely cause of the lower rate constant at 1409 K.

TABLE IV: Arrhenius Expressions for the Reaction of CN with Hydrocarbons and Hydrogen⁴

species	temp range, K	rate expression	technique ^b	ref	
H	292-1500	$(5.0 \pm 0.4) \times 10^{-11} \exp[(-2450 \pm 50)/T]$	LIF	с	Î
CH	292-1500	$[(1 \pm 2) \times 10^{-19}]T^{(2.64\pm0.24)} \exp[(+220 \pm 150)/T]$	LIF	this work	
-	260-400	$(1 \pm 0.5) \times 10^{-11} \exp[(-870 \pm 300)/T]$	LIF	10	
	all	$[4.8 \times 10^{-13}] T^{0.657} \exp(-2400/T)$	theory	35	
C ₂ H ₄	292-1140	$[(2 \pm 7) \times 10^{-19}] T^{(2.77 \pm 0.59)} \exp(+(900 \pm 300)/T)$	LIF	this work	
- 20	294-736	$(7.40 \times 10^{-15})T^{1.29} \exp(+258/T)$	LIF	5	
C,H,	292-1270	$[(2 \pm 3) \times 10^{-14}]T^{(1.22\pm0.20)} \exp[(+400 \pm 150)/T]$	LIF	this work	
- 3 8	294-736	$(2.15 \times 10^{-4})T^{1.14} \exp(+285/T) + (6.60 \times 10^{-13})T^{0.56} \exp(+327/T)$	LIF	5	

^a Listed uncertainties are $\pm 1\sigma$ from least-squares fits. ^bLIF = laser-induced fluorescence; KAS = kinetic absorption spectroscopy. ^c Balla, R. J.; Casleton, K. H., unpublished results.

We have fit the data, excluding the point at 1409 K, to a three-parameter expression as described for methane and ethane. The results for the fit are

$$k = [(2 \pm 3) \times 10^{-14}] T^{(1.22 \pm 0.20)} \exp[(+400 \pm 150)/T] \text{ cm}^3/(\text{molecule s})$$

The quoted parameter uncertainties are $\pm 1\sigma$. As with the methane and ethane data, the fit parameters are strongly correlated, leading to large uncertainties in the values of the estimated parameters. Similarly, the comparison between the fits and the experimental values, producing a fit standard deviation of about $\pm 10\%$, is much better than is suggested by the uncertainties in the parameters. These data can also be fit by a four-parameter, two-exponential model. While the data could also be consistent with the presence of a second, higher temperature process, the lack of data in this higher temperature regime prevents us from drawing any firm conclusions about the presence or nature of this process.

The recent experiments of Hess, Durant, and Tully⁵ provide results similar to ours for the temperature range 294-736 K, with rate coefficients about 10% higher than ours but within combined experimental errors. Their data are fit to the sum of two different three-parameter expressions for the rate coefficients, describing the reaction of CN with primary and secondary site hydrogen on the C_1H_8 . The higher temperatures in the experiments reported here result in only slightly greater curvature in the Arrhenius plot than can be extrapolated from their fit to their data.

As stated above, there are insufficient data to warrant a sixparameter, two-exponential fit to our data. This is particularly true considering the large amount of correlation among the fit parameters, which results in extremely large uncertainties in their values. However, we can obtain an estimate of the relative contribution of primary and secondary hydrogens to the CN disappearance rate constant by subtracting the ethane rate (due to reaction of the six primary hydrogens) from the propane rate (due to reaction of the six primary and two secondary hydrogens). The resulting rate for reaction of CN with secondary hydrogens decreases with increasing temperature from approximately 2.5 $\times 10^{-11}$ cm³/s per secondary hydrogen at room temperature to 1.8×10^{-11} cm³/s at 1000 K. This is similar in both magnitude and temperature dependence to the results obtained by Hess et al.5

There are at least 11 exothermic channels available to this reaction. The channels forming acetonitrile and propionitrile (CH₃CH₂CN) are the most exothermic. Unfortunately, it was not possible to determine a branching ratio for HCN/CH₃CN production due to spectral interferences in the DLA experiments. However, HCN was observed as a primary product of the reaction. No CH₃CN was observed even after multiple laser shots on a static gas sample, but, because of the interferences, only very large amounts of CH₃CN would have been observed. Based on our observations and the data in methane and ethane, it seems likely that HCN would be the dominant low-temperature product.

CN has often been called a pseudo-halogen because of its large electron affinity and the strong CN bond.³¹ Reactions of the alkanes with halogens have been studied at temperatures in the range 200-700 K.³² Three-parameter fits have been obtained for the reaction of Cl with CH_4 .^{33,34} A positive activation energy was observed for the Cl reactions, while we see a small negative activation energy for the analogous CN reaction. For Cl, the observed curvature in the data was attributed to the formation of a transition state, an inherently temperature-dependent process, and to quantum mechanical tunneling, whose contribution increases at lower temperatures for light-atom-transfer reactions. Since we observe no barrier to the CN + CH₄ reaction, tunneling is not believed to be present. The C_2H_6 and C_3H_8 reactions with Cl show little curvature over the range studied³² and have been fit to simple Arrhenius expressions. In the same temperature regime, our data for CN reactions can also be fit to simple Arrhenius expressions with very similar parameters. It is at higher temperatures that the CN reactions with ethane and propane show a large degree of curvature. The analogous Cl reactions have not been studied at these higher temperatures.

The CN reactions with alkanes display different Arrhenius behavior than is typically found in hydrogen abstraction reactions by diatomic radicals. The preexponential factors in the Arrhenius expressions (Table IV) and the room temperature rate coefficients (Table III) are unusually large for hydrogen abstraction reactions by diatomic radicals. In general, abstraction reactions have preexponential factors that are several orders of magnitude less than collision frequency, while reactions that occur by addition or insertion are nearly gas kinetic. By comparison, CN reactions have both preexponential factors and room temperature rate coefficients that are approximately 10³ faster than OH reactions and 10-100 times slower than CH. This large preexponential factor can occur in the presence of long-range electrostatic forces between molecules.³¹ In the CN plus hydrocarbon system, the forces are dipole-induced dipole and London dispersion forces created by the large electronegativity of the CN radical. This is consistent with considering CN as a pseudo-halogen. Theoretical calculations using a collision complex model based on the attractive potential described by Fairchild et al.36 confirm that these forces can combine to produce a long-lived complex that decomposes to yield a stable product by an elimination process and produce large preexponential factors. Sayah et al.³¹ also used a collision complex model to explain the reaction of CN with a wide variety of saturated and unsaturated hydrocarbons at room temperature.

Recently, Hess, Durant, and Tully⁵ have measured absolute rate constants for the reactions of CN with ethane, propane, and various deuterated analogues. Experiments were performed by using the laser photolysis/CW laser-induced fluorescence technique from 294 to 736 K. Assuming HCN to be the primary reaction product, these authors performed a transition-state

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calculation that agreed well with their experimental data. They also employ a "loose" transition state with very little perturbation of the alkane in going from the reactants to the transition state.

Conclusions

Rate coefficients for the reaction of CN with methane, ethane, and propane have been studied from 293 to 1500 K by using high-temperature photochemistry. This study represents the widest continuous temperature range over which rate constants for these reactions have been directly measured. In addition, these experiments are also the first to use direct methods to monitor the products of reactions of CN with hydrocarbons. All rate coefficients are independent of pressure and flow velocity. The rate coefficients are large and can be explained by the existence of long-range intermolecular attractive forces. The Arrhenius plots for these reactions are curved. In all cases, HCN is the dominant observable room temperature product, even though for ethane and propane lower energy products are possible. Both the curvature and the magnitude of the rate constants can be explained by a long-lived collision complex existing over the entire temperature range. However, the observed lack of any pressure dependence would indicate that the high-pressure limit was reached by 10 Torr of total pressure. In order to unambiguously determine the mechanism of these reactions, further calculations and additional experiments at 800-1200 K would help by establishing the curvature in this temperature regime.

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AIH Gas-Phase Reaction Kinetics

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The reactions of ground-state AlH ($^{1}\Sigma^{+}$) with O₂, H₂O, H₂, D₂, C₃H₈, C₂H₂, 2-butyne, C₂H₄ and 2-methyl-2-butene are investigated at 300 K. The AIH is produced by the photodissociation of triethylaluminum at 193 or 248 nm and detected by laser-induced fluorescence of the A ${}^{1}\Pi$ -X ${}^{1}\Sigma^{+}$ transition. Absolute bimolecular rate constants are obtained from AlH concentration decay profiles as a function of reactant gas concentration. The rate constants for oxygen containing reactants reported in units of cm³ s⁻¹ are (1.58 ± 0.15) × 10⁻¹² for O₂ and (3.09 ± 0.35) × 10⁻¹¹ for H₂O. For H₂ and D₂, we are unable to observe reactions with AlH at low pressures; we report an upper limit of 1×10^{-14} cm³ s⁻¹ at 20 Torr of total pressure. The reaction of AlH + D_2 is dependent on the total pressure; at 460 Torr we observe AlH depletion with a rate constant of $(1.4 \pm 0.2) \times 10^{-14}$ cm³ s⁻¹. The saturated hydrocarbon reactant, C₃H₈, also reacts with a rate constant <1 × 10⁻¹⁴ cm³ s⁻¹. Unsaturated hydrocarbons exhibit very rapid rates of reaction. C_2H_2 and the methyl substituted, 2-butyne species have rate constants of $(1.12 \pm 0.11) \times 10^{-10}$ and $(2.51 \pm 0.31) \times 10^{-10}$ cm³ s⁻¹, respectively. The C_2H_4 and methyl-substituted, 2-methyl-2-butene species have rate constants of $(2.21 \pm 0.19) \times 10^{-11}$ and $(1.5 \pm 0.17) \times 10^{-11}$ cm³ s⁻¹, respectively. Comparisons of AlH reaction rates are made with those of the isovalent BH species, Al atoms, and the isoelectronic Si atom.

Introduction

Scientific interest in the AlH diatomic radical is quite varied. It has astrophysical significance in that spectroscopic features have been observed in red-giant stars estimated to be at temperatures of 2000-4000 K^{1,2} and also in solar sunspots.³ There has been a report of its use as the active medium in a metal-hydride photodissociation laser operating in the visible spectral region.⁴ The molecular size of AlH is still tractable for theoretical calculations of the X ${}^{1}\Sigma^{+}$, A ${}^{1}\Pi$, and C ${}^{1}\Sigma^{+}$ electronic states and serves as a test of specific theoretical approaches.^{5,6} The interest in the combustion of metal-based propellants and explosives peripherally extends to the chemistry of small metal-containing species for a complete understanding of the chemical pathways. But perhaps the most practical reason to study the AlH radical has to do with its importance in the fabrication of electronic materials and other Al-coated surfaces. The AlH species is a

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photolytic product of several organometallic precursors used in laser-induced metal-organic vapor-phase epitaxy (MOVPE).⁷ These AlH-producing precursors include triisobutylaluminum (TIBAl), triethylaluminum (TEAl), and to a lesser extent trimethylaluminum (TMA); all are used in the production of Al-GaAs material.⁸ TMA, currently the most commonly used source of Al, produces carbon contamination in the films due to the strength of the aluminum-carbon bond in TMA.⁹ Gas-phase reactions in addition to surface reactions appear to influence the rate of carbon surface incorporation.¹⁰ As evidence for the difficulty of removing the final methyl group from TMA, ultraviolet excimer laser dissociation of TMA yields AlCH₃ as the primary molecular gas-phase product.⁷ In contrast, a different pyrolysis mechanism is operative for TEAl and TIBAl in which β -elimination occurs, leaving for instance $(C_2H_5)_2$ AlH in the former case. This mechanism occurs in successive steps to the AlH₃ product, which then decomposes to Al metal.⁹ Reductions in carbon incorporation have been achieved using TEA1. 11 Laser photolysis of TEAl produces the AlH as the primary molecular

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