Photometric and Mass Spectrometric Observations on the

Reaction of Hydrogen Atoms with Cyanogen

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The reaction is accompanied by a weak emission flame consisting of bands of the red and violet systems of CN. The intensity of CN emission at low cyanogen flows is proportional to [H]³/[H₂], as would be predicted by the proposed mechanism: $H + C_2N_2 \rightarrow HCN + CN$ (1); $CN + H_2 \rightarrow HCN + H$ (2); H +(3). The rate constant k_1 at room temperature is found to be $(8.6 \pm 3.0) \times 10^{-16}$ $H + CN \rightarrow H_2 + CN^*$ cm^3 molecule⁻¹ sec⁻¹. This is consistent with a value of about 100 kcal for the heat of formation of the CN radical. With cyanogen in excess, reaction 2 competes with polymer formation, initiated by $^{1}CN + C_{2}N_{2} \rightarrow$ (4); the value of k_4 , estimated from the point of onset of polymer formation, is about 1×10^{-14} C_3N_3 cm^{3} molecule⁻¹ sec⁻¹.

Introduction

Haggart and Winkler² showed that the reaction of H atoms with cyanogen in the presence of excess H_2 involves the chain process

$$H + C_2 N_2 \longrightarrow HCN + CN \tag{1}$$

$$CN + H_2 \longrightarrow HCN + H$$
 (2)

Reaction 1 is stated to be fairly fast at room temperature.³ For reaction 2 Hartel and Polanyi⁴ estimated a value of about 7 kcal for the activation energy; this is reasonably consistent with Iwai, Pratt, and Broida's estimate⁵ of 3×10^{-14} cm³ molecule⁻¹ sec⁻¹ for the rate constant k_2 at room temperature. In a recent study of the H + ICN reaction in this laboratory⁶ it was shown that the observed CN luminescence was excited by the termolecular process

$$H + H + CN \longrightarrow H_2 + CN^*$$
(3)

The present photometric observations have shown that reaction 3 is also responsible for the blue-white luminescence that accompanies the $H + C_2N_2$ reaction, while both the photometric and the mass spectrometric observations are consistent with a mechanism of HCN production based on reactions 1 and 2, with the addition of polymer-forming reactions when C₂N₂ is in excess. Our mass spectrometric studies lead to a value of 8.6×10^{-16} cm³ molecule⁻¹ sec⁻¹ for the rate constant k_1 at room temperature. On the assumption of a normal preexponential factor of about 10^{-10} , the rate constant found for reaction 1 is consistent with the "low" value of about 100 kcal given by a number of workers⁷ for the heat of formation of the CN radical.

Experimental Section

The photometric⁶ and mass spectrometric⁸ apparatus and procedures were as previously described. Experiments were carried out at total pressures near 1 Torr. For the photometric studies H-atom concentrations were measured with an isothermal probe,⁶ while in the mass spectrometric experiments the $H + NO_2$ titration⁹ was used. Emission spectra were recorded with a McPherson Model 218 0.3-m monochromator, with an EMI 9558Q photomultiplier and a Keithley high-speed picoammeter. Low-resolution intensity measurements were made with a 1P21 photomultiplier plus a Corning 7-54 filter. Hydrogen was drawn from an Elhygen electrolytic generator (total impurities less than 10 ppm), or from a tank of commercial electrolytic hydrogen, via a tube of heated copper wool and a liquid air trap. The hydrogen was normally diluted, prior to the microwave discharge, with a large excess of either Matheson helium or welding-grade dry argon. The inert gases were purified by passage over heated BTS catalyst followed by successive towers containing sulfuric acid and P_2O_5 . Matheson cyanogen (stated purity 99.1%, main impurities being HCN and CO_2 , with 0.04% of CNCl and a trace of $\mathrm{N}_2)$ was used in the photometric experiments without further purification. For the mass spectrometric studies it was fractionated with a LeRoy still.

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Results and Discussion

The blue-white reaction flame, consisting of bands of the red and violet systems of the CN radical, with no tail bands evident, typically extended along the full 50-cm length of the reaction tube (linear flow velocity about 8 m sec^{-1}) when H atoms were in excess. When the cyanogen flow was gradually increased the intensity increased quite rapidly until an optimum flow was reached. After about 30 sec of operation at the optimum flow rate the flame shortened, the CN intensity fell by about two orders of magnitude, and a weak greenish luminescence from a layer of polymer on the walls⁶ became evident. The spectrum of the bluewhite emission differed from the H + ICN flame, in that the ratio of violet to red intensities was greater with C_2N_2 , and the intensity distribution among the bands showed marked differences in the population of vibrational levels of the upper state. This is illustrated in Figure 1 for the (v,v) sequence of the violet system. Since we are attributing the CN excitation to the same process in both cases, namely reaction 3, it is necessary to assume either that there is some specific process leading to rapid vibrational relaxation of excited CN in the H + ICN system, or that the ground-state CN radicals produced by reaction 1 differ from those produced in the H + ICN system in that they already possess some vibrational excitation.

The formation of CN polymer is believed to be initiated by the reaction¹

$$CN + C_2N_2 \longrightarrow C_3N_3$$
 (4)

Hence the steady-state concentration of CN radicals is given by

$$[CN] = k_1[H][C_2N_2]/(k_2[H_2] + k_4[C_2N_2])$$
(5)

The appropriate value of k_2 for insertion in this expression may be higher than the room temperature figure of 3×10^{-14} cm³ molecule⁻¹ sec⁻¹ because of the presence of vibrationally-excited H₂ from the discharge.¹⁰ Under conditions where polymer formation can be neglected this expression reduces to k_1 [H][C₂N₂]/ k_2 [H₂], so that the intensity of CN emission due to reaction 3 becomes

$$I_{\rm CN} = k_1 k_3 [\rm H]^3 [\rm C_2 N_2] / k_2 [\rm H_2]$$
(6)

Hence, under conditions where sufficient time has elapsed for the steady state to be established with respect to [CN], but the actual consumption of C_2N_2 is small, the effect of varying [H] should be such that a graph of $I_{\rm CN}$ against [H]³/[H₂] is a straight line through the origin. An experimental test of this result is shown in Figure 2; a good linear dependence of $I_{\rm CN}$ on [H]³/[H₂] is found, except at high values of [H] where the consumption of C_2N_2 is likely to be important.

We have noted that as the flow of cyanogen was increased a point was reached at which the flame suddenly shortened and the buildup of a polymer deposit on the



Figure 1. Low-resolution scan showing relative intensities of emission bands in the (v,v) sequence of the CN violet system: (A) H + ICN flame; (B) H + C₂N₂ flame.



Figure 2. Graph of CN emission intensity vs. $[H]^{3}/[H_{2}]$ at t = 30 msec: $[C_{2}N_{2}] = 3.4 \times 10^{13}$, $[H_{2}] \sim 1.7 \times 10^{15}$, $[H] \sim 1 \times 10^{15}$. [H] was varied by varying the power supplied to the discharge.

walls became noticeable. It may be assumed that at this point the rates of removal of CN by reactions 2

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[Ar]	$[H_2]$	$10^{3} [C_{2}N_{2}]_{0}$	$10^{3} [C_{2}N_{2}]_{t}$	103[H]0	t	10 ¹⁶ k1
0.523 0.1	0.154	7.15	6.70	6.70	165	8.55
		12.51	11.7			8.7
		8.94	8.37			8.7
1.85 0.500	0.500	11.76	9.24	18.7	550	6.68
		6.30	4.70			8.1
		9.49	7.31			7.2
0.946 0.209	0.209	12.22	10.46	23.07	273	6.8
		23.66	20.66	24.27		5.8
		12.66	10.14	26.05		8.8
		12.98	10.51	22.21		9.9
		13.26	12.60	4.517		11.6
		3.645	2.804	25.68		10.6
		3.493	2.775	21.68		11.0
1.102	0.024	3.74	3.55	8.77	325	5.2
	0.076	13,44	10.62	20.57		6.3
1.152	0.076	5,02	4.155	22.13		7.43

Table I: Evaluation of k_1 :^a Partial Pressures in Torr. Times. t. in Milliseconds

and 4 were comparable, so that if one of the two rate constants is known an estimate can be made of the other. In two typical determinations of the point at which the flame began to shorten the reactant concentrations (in particles cm⁻³) were $[H_2] = 8.6 \times 10^{14}$, $[C_2N_2]$ = 3.4 × 10¹⁴, [H] = 1.7 × 10¹⁵, and [H₂] = 4.3×10^{15} , $[C_2N_2] = 8.6 \times 10^{14}$, $[H] = 3.8 \times 10^{15}$, respectively. Equating $k_2[H_2]$ with $k_4[C_2N_2]$, and taking $k_2 = 3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, these determinations give k_4 values of 7.4 \times 10⁻¹⁴ and 1.4 \times 10^{-13} , respectively. Both values are considerably larger than the figure of 3.6 \times 10⁻¹⁵ given by the Arrhenius expression of Paul and Dalby¹ at 300°K. The value of 3 \times 10⁻¹² estimated by Boden and Thrush¹¹ for k_4 at temperatures near 600°K is also greater, by a factor of about 150 in this case, than the corresponding value derived from Paul and Dalby's Arrhenius expression. Our estimates of k_4 , and that of Boden and Thrush, should be reliable to within an order of magnitude; the observed discrepancies tend to confirm Boden and Thrush's suggestion that reaction 4 is partly heterogeneous.

The rate of reaction 1 at 300°K was determined mass spectrometrically in a flow system in which the walls were poisoned with phosphoric acid. The flow system was designed for the study of reactions with rate constants greater than about 10^{-14} cm³ molecule⁻¹ sec⁻¹, so that for the H + C₂N₂ reaction it was necessary to throttle down the flow speed (to about 100 cm sec⁻¹) by almost closing the lead to the pump. Preliminary measurements with no discharge showed that the reaction of C₂N₂ with H₂ could be neglected. From the data obtained using the microwave discharge, values of rate constants were calculated for reaction 1, on the assumption that the overall stoichiometry was

$$H_2 + C_2 N_2 \longrightarrow 2HCN$$
 (7)

(*i.e.*, that H atoms were regenerated by reaction 2) and also for the termolecular reaction

$$H + H + C_2 N_2 \longrightarrow 2HCN \tag{8}$$

with no regeneration of H. The "rate constants" obtained for reaction 8 varied widely, and gave a mean value of 2×10^{-30} cm⁶ molecule⁻² sec⁻¹ which is very large for such a reaction. On the other hand the values obtained for k_1 (see Table I) were reasonably consistent over a considerable range of initial [H] and $[C_2N_2]$ values. The mean value found for k_1 was 8.2 \times 10^{-16} cm³ molecule⁻¹ sec⁻¹, with a standard deviation of 1.8×10^{-16} . The estimated error of the results is about 1.5 times the standard deviation. Systematic errors in the k_1 values would be introduced by the recombination of hydrogen atoms, which could have amounted to as much as 20% at t = 500 msec and not more than 10% elsewhere in Table I. This would cause the k_1 values to be too low by 5% at most. The H-atom concentrations might also have been overestimated by the NO₂ titration, which is subject to error in the presence of excess H_2 .¹² A computer simulation of the titration reaction using the known rate constants^{7,12,13} showed that under the typical conditions of our experiments ([H] = 0.02 Torr, [H₂] = 0.15 Torr) the concentration of [H] would have been overestimated by less than 5%. As a further check we measured the reduction in peak height at mass 2 when the discharge was activated, with and without NO₂ present, and found no significant variation except under the worst

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conditions of excess H₂, when an error amounting to a change of 5% in the value of k_1 may have been introduced. Making an allowance for these sources of error, we give our final k_1 value as $(8.6 \pm 3.0) \times 10^{-16}$ cm³ molecule⁻¹ sec⁻¹.

The activation energy of reaction 1 is an upper limit for the endothermicity of this reaction. If a preexponential factor of 10^{-10} is assumed the above value of k_1 is found to correspond to a value of not more than 99.6 kcal mol⁻¹ for the heat of formation of the CN radical (for the other heats of formation we use the 0°K values listed in Davis and Okabe's Table IV;⁷ the use of room temperature values would make a difference of at most 1 kcal in the calculated heat of formation of CN). A larger value of the heat of formation would appear to require an unreasonably large preexponential factor; for example, if the heat of formation is raised to 102 kcal the preexponential factor becomes 5×10^{-9} . Thus it is difficult to reconcile this k_1 value with the recent determination by Berkowitz, Chupka, and Walter¹⁴ which gave a value of 105.5 kcal. The kinetic data of Boden and Thrush¹¹ also require a heat of formation near 100 kcal. On the other hand, our observation that reaction 1 is quite slow appears to dispose of the main argument given by Safrany and Jaster³ in support of the "ultra-low" figure of 92.5 kcal for the heat of formation of CN.

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Isomerization of Vibrationally Excited 3-Methyl-1-buten-1-yl Radicals

via Hydrogen Atom Migration. Quantum Statistical Weight Effect¹

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The unimolecular rate constant for the isomerization by 1,4 hydrogen atom migration of the 3-methyl-1-buten-1-yl radical was measured. The radicals were generated with an average excess vibrational energy of ~ 34 kcal mol⁻¹ by the addition of isopropyl radicals to acetylene at 53°. The average rate constant was 4.1 \times 10⁸ sec⁻¹. This rate constant, when compared with previous results for *n*-pentyl isomerization, provides a demonstration of the variation of elementary rate constants that occurs when the vibration-internal rotation frequency pattern is altered by substitution of a double bond for a single carbon-carbon bond. The best agreement between the rate constant as calculated by the RRKM theory and the experimental result was found when the threshold energy was chosen to be 17.1 kcal mol⁻¹. Other kinetic data reported are: the rate constant for addition of isopropyl to acetylene, $k_1 = 10^{11.80} \exp(-7600/RT)$ cm³ mol⁻¹ sec⁻¹; $\Delta(i$ -Pr, 1-penten-4-yl) = 0.4; $\Delta(1$ -penten-4-yl, *i*-Pr) = 0.3. The formation of benzene in this system is discussed.

Introduction

The isomerization of alkyl radicals via hydrogen atom migration has recently received much attention in both equilibrium² and nonequilibrium^{3,4} reaction systems. Isomerization of alkenyl radicals offers a novel and important comparison to the study of alkyl radical isomerization. For the same or similar activated complexes the principal feature which determines the relative rates of two reactions in nonequilibrium systems, according to the RRKM formulation of unimolecular reactions, is the density of eigenstates, $N^*(E)$, of the molecule at the energy of interest.⁵ Alterations in molecular structure which change the molecular vibration-internal rotation frequency pattern, but do not exert an appreciable mechanistic effect, are called quantum statistical weight effects. Pre-

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