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DETERMINATION OF THE RATE OF FORMATION OF HCN

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ABSTRACT

Nitric oxide is a major air pollutant arising from fossil fuel combustion, yet the fuel contribution to its formation is uncertain. Since, in combustion, fossil fuels undergo disintegration before oxidation takes place, the study of the pyrolysis of a model constituent of fossil fuels can shed light on NO formation. The rate of inert pyrolytic disappearance of pyridine and the rate of formation of the principal Nitrogen-containing pyrolytic product, HCN, was studied in an inert atmosphere. The rate constant for the formation of HCN and its temperature dependence were determined.

A. Introduction and Statement of the Problem

The reduction of the air pollution generated by the burning of fossil fuels is a serious and difficult task facing society today. With the cleaner-burning fuels such as natural gas soon to be replaced by the more problematic fuel, coal, as our main source of energy, the exact nature of this combustion process must be fully understood so that ways can be found to minimize the noxious side products of this process.

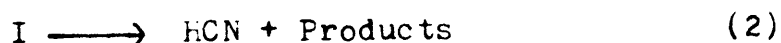
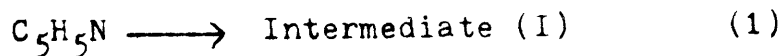
Various oxides of nitrogen are among the chief contributors to combustion-caused air pollution. NO_2 increases lung tissue fluid retention and excretion in humans and has emphysema-like effects on rats.¹ Nitric oxide (NO) has an affinity for hemoglobin similar to that of carbon monoxide. Other effects undoubtedly exist. Thus it can be seen that the formation of nitrogen oxides during combustion is a health hazard and needs to be controlled.

There are two possible sources of NO in combustion. The formation of NO from atmospheric nitrogen has been (apparently) satisfactorily described² but an equally important process, the formation of NO from fuel nitrogen, has not. Even the reactions which contribute to NO formation are not known, much less the rate constants for the reactions. Since pyridine is representative of the nitrogen-containing components of fossil fuels,^{3,4} a study of the kinetics and mechanisms of the pyrolysis of pyridine would shed light on this little-understood process of NO formation. This project, sponsored by the United States Energy Research and Development Administration, was conducted by Dr. Thomas Houser, Western Michigan University.

It has been found⁵ that HCN may be the key intermediate in the

formation of NO. Therefore, the rate and mechanism of formation of HCN in the pyrolysis of pyridine was studied using a flow system operation at atmospheric pressure and incorporating a quartz stirred-flow reactor which was heated by a surrounding furnace. This stirred-flow technique allows greater freedom in the selection of reaction conditions and permits easier interpolation of kinetic data from complex order reactions. Helium was used as an inert carrier gas and a motor driven syringe was used to inject pyridine into the stream.

The formation of HCN from pyridine is thought to be a two-step process:



The rate of step 2 is given for a stirred-flow reactor⁶ by

$$d(\text{HCN})/dt_c = (\text{HCN})/t_c = k_2(I)$$

where k_2 is the rate constant for reaction 2 and t_c is the contact time (defined as the residence time t_c of the molecule in the stirred-flow reactor itself). If it is assumed that (I) is proportional to the difference between the change in pyridine concentration and the HCN concentration evolved, then

$$k_2 = \rho/t_c(1-\rho) \quad (3)$$

where ρ is the measured molar ratio of HCN formed to pyridine consumed.

Therefore, a suitable method for determining the amount of HCN formed in the inert pyrolysis of pyridine was needed in order to ascertain the rate constant k_2 and its temperature dependency.

B. Selection of a Method for the Determination of HCN

At first glance there are a bewildering number of different ways to quantitatively determine cyanide ion (CN^- is the form of HCN analyzed in most methods, though a few first convert HCN to thiocyanate and determine it). Streuli and Averell⁷ alone list more than eighty-two different methods, dating from 1851. Quickly, though, schemes can be eliminated as being too expensive or time-consuming. Titrimetry was ruled out due to the delicate end-point determinations usually involved and because the best-known Liebig method⁸ involved a second complex to complicate the end-point further. Also, titrimetric determinations tend to be lengthy and not allow several samples to be tested in short order.

Colorimetric methods rely on the absorption of a bandwidth of ultraviolet or visible light by a particular species which may be the species of interest itself or the product of some known stoichiometric reaction with added reagents. Once the solutions have been prepared measuring their absorbances is a trivial matter. Determining a standard curve using known quantities of the species of interest allows correlation of absorbance and concentration.

Many colorimetric determinations of cyanide have been described. Choice is dictated by the specificity of the method for the species of interest, lack of interference from other species present, the stability of the developed color, the reproducibility of results, and the simplicity of the manipulations. The picric acid method⁹ meets these criteria. While interferences are mainly due to other volatile reducing compounds (such as sulfide, sulfur dioxide, acetone,

and formaldehyde) equal amounts of these do not produce as great a color intensity as that produced by cyanide. Also, these compounds are not present in the reactor effluent in any significant amounts. The color developed is stable, the procedures are simple and brief, the reagents are easily prepared and stable, and the method has adequate sensitivity. Moreover, the accuracy is within 2% of the actual value. The reaction is



C. Analytical Work

1. Preparation of Standard Curve¹⁰

a. Reagents

- 1). 1% picric acid, by weight in H₂O (acid is 10-15% H₂O).
- 2). KCN--Amount of KCN equivalent to 1.000g HCN is weighed into a 1-liter volumetric flask and diluted with H₂O. A 100ml aliquot of this diluted to 1 liter gives a standard solution with HCN concentration of 100ppm.
- 3). 0.5 M Na₂CO₃

b. Procedure

Aliquots containing 10, 20, 50 and 100ml of the cyanide solution are pipeted into separate 100ml volumetric flasks, and diluted with H₂O. 5ml aliquots of these solutions are pipeted into dry 100ml volumetric flasks. To each of these is added 5.0ml of the Na₂CO₃ solution followed by 5ml of 1% picric acid solution, to make a total volume of 15ml. Immediately after addition of picric acid, im-

merse flasks in boiling water bath for 5 min \pm .5 min. The time and volume are important for reproducible results. Remove the flasks from bath, immediately dilute to mark, cool to room temperature to stop the reaction, and adjust the volumes. The absorbance is read against distilled water @ 520 μ within 30 hours.

c. Measurement of Absorption of Standard Solutions

Instrument used: Beckman Model B UV-Visible Spectrometer. Blank had a 106% transmittance while distilled water had 100%T. Longer wavelengths were tried but no decrease in this effect was seen, so the standard solutions (and all subsequent solutions) were read against a blank consisting of Na₂CO₃, H₂O, and picric acid in amounts and treatment identical to the standard solutions. The following data is plotted in Figure 1.

<u>(HCN), eq. moles/liter</u>	<u>Absorption</u>
1.85 x 10 ⁻⁵	.057
3.70 x 10 ⁻⁵	.115
9.25 x 10 ⁻⁵	.334
1.85 x 10 ⁻⁴	.646

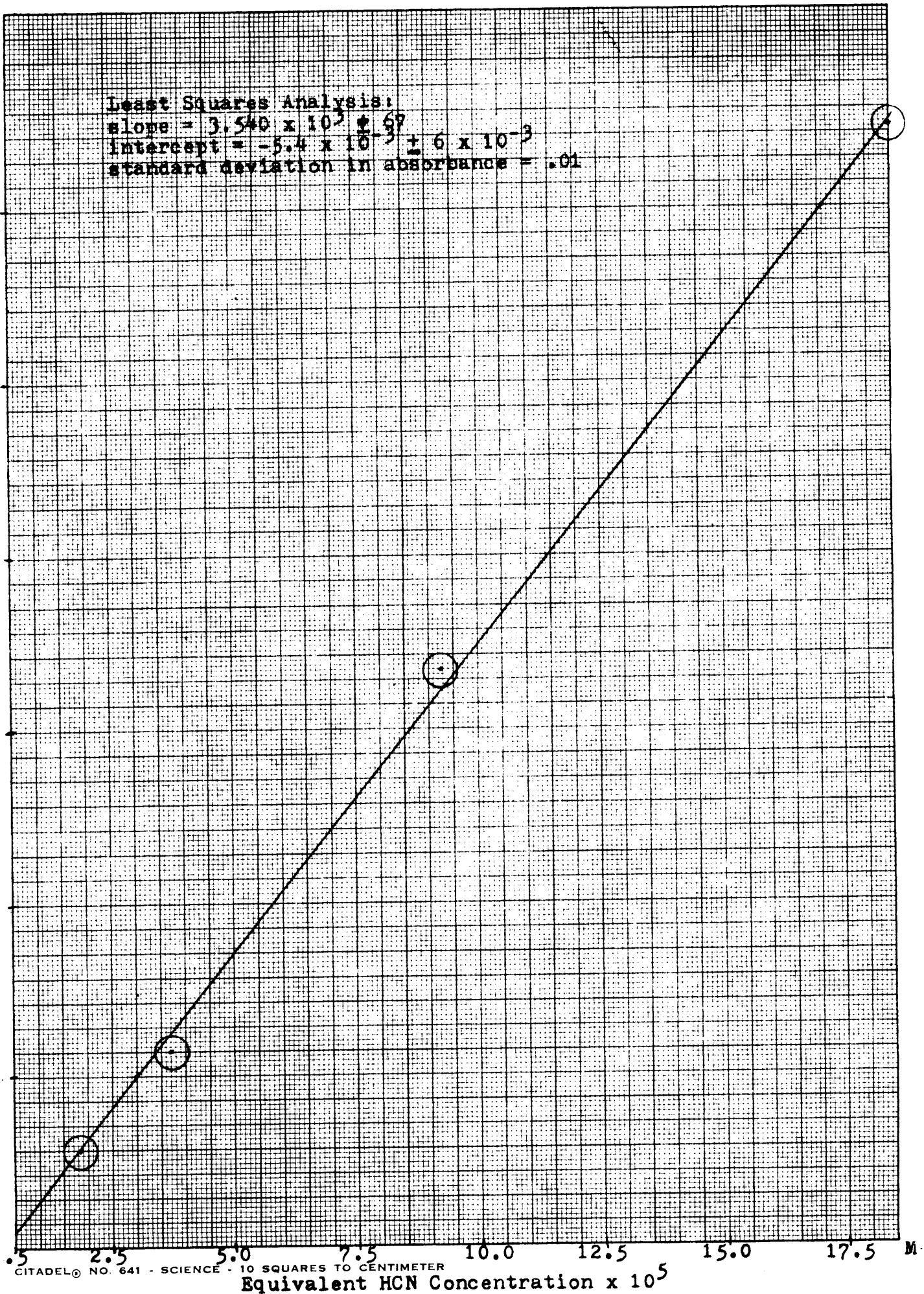
Least-squares analysis of this data (including blank) yields; slope = 3.540 x 10³, intercept = -5.356 x 10⁻³

2. Interferences

Some possible sources of interference were discussed above. Since high amounts of pyridine (about ten times that of HCN) are present in the reactor effluent and are soluble in the solution used

Standard Curve for the Determination of Cyanide

Least Squares Analysis:
slope = $3.540 \times 10^{-3} \pm .67$
intercept = $-5.4 \times 10^{-3} \pm 6 \times 10^{-3}$
standard deviation in absorbance = .01



CITADEL® NO. 641 - SCIENCE - 10 SQUARES TO CENTIMETER
Equivalent HCN Concentration x 10⁵

to collect the HCN, the effect of this CN-like molecule was ascertained. Two trials were conducted: 1) Solutions of pyridine, picric acid and Na_2CO_3 were assembled in precisely the same manner as the solutions prepared for the standard curve and tested for absorbance (with pyridine concentrations of 6 and 19ppm). Allowing for experimental tolerances, no absorbance was seen. 2) Solutions of KCN, pyridine, picric acid and Na_2CO_3 were prepared as above, using HCN/pyridine concentration ratios of 1/10, and the absorbances measured. In the range of equivalent HCN concentrations from 0.5 to 5ppm, no substantial deviations from standard curve behavior were noted. Thus, it was concluded that pyridine did not interfere with the cyanide determination.

3. Collection and Analysis of HCN

The gaseous exhaust of the stirred-flow reactor was bubbled through a basic aqueous solution to trap the HCN in the stream in the form of CN^- , using a fritted disk to aid in dissolution of the cyanide. A single bubbling unit was found sufficient since a second bubbler in series with the first trapped little if any additional cyanide. Typically, 125ml of 0.50 M Na_2CO_3 was the basic solution used to trap the HCN over a 1000 second period. This was then diluted precisely to concentrations commensurate with the range of the calibration curve and the spectrometer. For example, the 125ml of carbonate (with its dissolved CN^-) was diluted first to 250ml, then 10ml of this was pipeted into 90.0ml of 0.25 M carbonate solution. Ten ml of this solution was then reacted with 5.0ml of the

same picric acid solution used in the calibration procedure, in the same manner. A blank was similarly prepared and the sample was then compared against the blank to determine its relative absorption of visible light. Since the molarity of the Na_2CO_3 in the picrate-cyanide reaction mixture to be measured had to be kept constant for consistent data, the concentration of the carbonate in the bubbler was varied as the dilution procedure varied to compensate for wide variations in cyanide concentration at the different pyrolysis conditions studied.

4. Calculation of k_2

The absorbance of the above solution was then referred to the calibration curve in order to determine the concentration of CN^- in the solution analyzed. This value was then multiplied by a factor to compensate for the dilution of the HCN originally collected, to arrive at a value for the number of moles of HCN evolved per liter of collecting solution in the 1000 sec collection period.

The number of moles of pyridine injected into the stream to pyrolyze was found by calibration of the Sage syringe driver.¹⁰ A dial on the instrument with a linear scale was used to vary the rate of injection of pyridine into the system. The volume of liquid ejected by a syringe attached to the driver over a time period for a given dial number was measured, and a constant called "dial factor" was determined such that

$$\text{Injection rate (mmoles/sec)} = (\text{dial factor})(\text{dial no.})$$

For a 1cc syringe, dial factor = 2.02×10^{-5} , while for a 2cc syringe, dial factor = 6.79×10^{-5} mmoles/sec. The relative amount

of pyridine consumed for each pyrolysis was determined by diverting the stirred-flow reactor effluent into a chromatographic column immediately prior to collection of HCN. The column separated the pyridine and directed a recorder to register relative amounts of pyridine graphically. By comparison of the stream before the reactor with the effluent during pyrolysis, the per cent reaction of pyridine could be ascertained. Thus

$$\text{Moles pyridine consumed} = (\% \text{ reaction})(\text{dial factor})(\text{dial no.})$$

Next, the ratio $\rho = \text{moles HCN produced} / \text{moles pyridine consumed}$ was calculated, and subsequently k_2 using equation 3.

C. Tabulation of Results

See table 1.

D. Comment

The determined values of k_2 (which exhibit a large scatter) show no significant trend with concentration or contact time and are consistent with a two-step consecutive reaction, the second step of which is first order (the first step is apparently autocatalytic¹⁰). An Arrhenius treatment of the average values of k_2 gives the temperature dependence of k_2 as

$$k_2 = 10^{11.0 \pm 1.4} \exp(-63,400 \pm 7,600/RT) \text{ (sec}^{-1}\text{)}$$

where R is the gas constant and T is the temperature in degrees Kelvin.¹¹

Since a typical combustion temperature is 1800°C one may wonder about the value of rate constants being determined at significantly lower temperatures. Because fuel undergoes pyrolysis at lower temperatures before oxidation occurs at the elevated temperatures,

knowledge of the mechanisms and rate constants of this initial step allows a better grasp of the overall process.

Table 1
RATE OF HCN FORMATION

Temp.	Initial Conc. (Mole % Pyridine)	Contact Time (sec)	Fraction Reacted (%)	ρ (HCN/C ₅ H ₅ N)	k_2 (sec ⁻¹)	
900°C	0.5	1.0	10	.210	.266	
	1.0	1.0	16	.118	.134	
	0.25	2.0	21	.138	.080	
	0.5	2.0	21	.294	.208	
	1.0	2.0	29	.184	.113	
	2.0	2.0	37	.192	.119	
	0.5	4.0	39	.324	.120	
	1.0	4.0	44	.295	.105	
	2.0	4.0	43	.363	.142	
	1.0	8.0	57	.394	.081	
	2.0	8.0	49	.479	.115	
					$\bar{k}_2 = .135$	
	950°C	1.0	0.5	25	.235	.62
		2.0	0.5	46	.122	.28
0.5		1.0	31	.412	.70	
1.0		1.0	40	.520	1.08	
2.0		1.0	59	.247	.33	
0.5		2.0	46	.553	.62	
1.0		2.0	54	.416	.36	
2.0		2.0	64	.427	.37	
1.0		4.0	70	.593	.36	
2.0		4.0	66	.627	.42	
					$\bar{k}_2 = .51$	
1000°C		0.5	0.5	39	.43	1.51
		1.0	0.5	50	.33	.99
	2.0	0.5	57	.34	1.03	
	0.5	0.5	43	.37	1.17	
	2.0	0.75	66	.47	1.18	
	0.25	1.0	43	.48	.92	
	0.5	1.0	54	.52	1.08	
	1.0	1.0	63	.52	1.08	
	2.0	1.0	76	.49	.96	
	2.0	1.0	80	.52	1.08	
	1.7	1.7	84	.64	1.05	
	0.5	2.0	67	.64	.89	
	1.0	2.0	77	.75	1.50	
	2.0	2.0	76	.73	1.35	
					$\bar{k}_2 = 1.13$	

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