FOSSIL ENERGY

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FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

Progress Report for the Period
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OBJECTIVE AND SCOPE

One of the major scientific problems confronting society today is the reduction and control of air pollutants. The emission of NO and other oxides of nitrogen from various combustion devices is a serious contributor to that pollution. The source of NO during the combustion process may be atmospheric nitrogen or nitrogen-containing compounds in the fuel. In order to predict NO emission for the formulation of suitable analytical models, it is necessary to have accurate kinetic data and a reasonable reaction mechanism for the formation of NO.

The objective of this research program is to obtain kinetic and product distribution data from which a mechanism may be proposed for the formation of NO from fuel nitrogen. Specifically, the kinetics of the pyrolysis and oxidative pyrolysis of pyridine (since it is representative of the nitrogen-containing components of fossil fuels) will be studied. In addition, similar oxidative studies will be made on quinoline, to determine the extrapolatability of the results obtained with pyridine to more coal-like structures. The oxidation of volatile, nitrogen-containing pyridine pyrolysis products, e.g. HCN and vinylcyanide, will also be carried out to help elucidate the mechanism of NO formation.

The experimental approach will involve the use of a stirred-flow reactor to obtain differential rate data which will aid in interpretation of complex kinetic data. On-stream mass spectrometric and gas chromatographic monitoring of products and reactants as well as chemiluminescent and specific ion electrode measurements will be used to obtain the data.

SUMMARY OF PROGRESS

Task 1. It was necessary to again revise the papers on the kinetics of pyridine pyrolysis after which they were accepted by the International Journal of Chemical Kinetics. The revised consideration of the rate of formation of HCN required an algebraic derivation to produce a new rate equation. If it is assumed that a fraction (α) of the decomposed pyridine forms an intermediate, a fraction of which (β) is capable of reacting further to form HCN, and that that formation is first-order in intermediate, the following rate equation describes the data

$$\rho/t = k_b\alpha\beta - k_b\rho$$

where ρ is moles HCN formed/mole pyridine decomposed, t is contact time and k_b is the first-order rate constant for the formation step. In addition, it was shown that since ρ was independent of initial pyridine concentration, the formation step was necessarily first-order. The Arrhenius parameters for k_b were 39.5 kcal/mole and 6.8 for E_a and log A (sec^{-1}) respectively. At 950 and 1000 C it was found that $\alpha\beta$ product was one, indicating all the pyridine could form HCN given enough time to react, whereas at 900 C the maximum HCN formed would be only about 60% of the pyridine decomposed. Finally, it was determined that the fraction of decomposed pyridine which can form HCN at a given time ranged from 0.16 to 0.77, indicating a significant concentration of intermediate builds up at all conditions. No volatile product found in the pyrolysis is close to that range of yields, thus the precursor to the HCN must react further on leaving the reactor.

Task 2. The paper on the Oxidation of Cyanogen was accepted by Combustion Science and Technology.

DETAILS OF TECHNICAL PROGRESS

Task 1

No new data were obtained during this period, however, further revisions were requested for the papers previously written. With these revisions the papers, "Pyrolysis Kinetics of Pyridine" and "Rate of Formation of HCN during Pyridine Pyrolysis" were accepted by the *International Journal of Chemical Kinetics*. The major revision in the latter paper required additional derivations with less restrictive assumptions which led to a new and interesting interpretation of the data and equations that had been reported previously (1,2). The following is a description of this reinterpretation.

The kinetic data are reported as the ρ (moles HCN formed/mole pyridine decomposed) value dependencies on initial concentration of pyridine (Table 1), and on contact time (Table 2). The ρ values increase steadily with reaction time, indicating a consecutive mechanism. These spectophotometric data (method in 3) are consistent with the semi-quantitative mass spectrometric data which indicated that the ion current for the m/e 27 ion per unit reaction increased with reaction time. This was not observed for the m/e 26 and 25 ions, which were primarily due to C_2H_2; these gave a constant ion current per unit reaction indicating that C_2H_2 was a product from the initial step or steps of pyridine pyrolysis. The ρ values appear independent of initial pyridine concentration, which indicates that the reaction producing HCN is first-order in intermediate species. If this were not a valid assumption, it would be expected that the ρ values would increase or decrease with initial concentration if the order were greater than or less than one respectively. This will be demonstrated more quantitatively later. It should be noted that the evolution of HCN reported by Axworthy, et al. (4) agrees reasonably well with the current value at similar conditions. They report an average ρ of .39 at about 960 C and one sec., which compares favorably with the current average of .33 at 950 and one sec.

Table 1

ρ* Dependence on Initial Concentration

Initial Concentration (mole % C_5H_5N)	Contact Time (sec)	Fraction Pyridine Reacted (%)	ρ
	900 °C		
0.25	2.0	21	.14
0.5		21	.29
1.0		29	.18
2.0		37	.19
0.5	4.0	39	.32
1.0		44	.30
2.0		43	.36
	950 °C		
0.5	2.0	46	.55
1.0		54	.42
2.0		64	.43
	1000 °C		
0.5	0.5	39	.43
0.5		43	.37
1.0		50	.33
2.0		57	.34
0.25	1.0	43	.48
0.5		54	.52
1.0		63	.52
2.0		76	.49
2.0		80	.52

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*ρ Ratio of moles HCN formed/mole pyridine decomposed.

Table 2

Time Dependence of ρ

Contact Time, t (sec)	Average ρ*	ρ/t	k_b* (sec^{-1})	$\alpha\beta$*
		900 °C		
1.00	.16 ± .05	.16		
2.00	.20 ± .05	.10	.30 ± .09	.60 ± .18
4.00	.33 ± .02	.082		
8.00	.44 ± .04	.055		
		950 °C		
0.50	.18 ± .06	.36		
1.00	.33 ± .08	.33	.492 ± .065	.95 ± .13
2.00	.47 ± .06	.24		
4.00	.61 ± .02	.15		
		1000 °C		
0.50	.37 ± .03	.74		
0.75	.47	.63		
1.00	.51 ± .02	.51	1.14 ± .11	.99 ± .10
1.70	.64	.38		
2.00	.71 ± .04	.35		

E_a* 39.5 ± 3.4 (kcal/mole)

Log A* 6.81 ± .61

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*The ± values on ρ are average deviations, all others are one standard deviation.

The following global reaction scheme is used to evaluate the data, recognizing that reaction (a) is a complex series of steps which has associated with it a complex rate equation (5) and that reaction (b) may or may not be an elementary reaction. In reaction (a), pyridine decomposes to one or more intermediates. It is assumed that a fraction (α) of the decomposed pyridine forms an intermediate, a fraction of which (β) is capable of reacting further to form HCN and hydrocarbons in step (b).

$$C_5H_5N \longrightarrow \text{Intermediates A + B + etc.} \tag{a}$$

$$A \longrightarrow \text{HCN + Hydrocarbon and Nitrogeneous Products} \tag{b}$$

The rate of a first-order step (b) in a stirred-flow reactor is given by eq. 1 (6)

$$d(HCN)/dt = (HCN)/t = \beta k_b(A) \tag{1}$$

where t is the contact time. Using the above assumptions, the concentration of intermediate which forms HCN is given by eq. 2

$$(A) = \alpha X - (HCN)/\beta \tag{2}$$

where X is the concentration of pyridine decomposed, and since $\rho = (HCN)/X$, the rate equation can be rewritten

$$\text{rate} = (HCN)/t = k_b\alpha\beta(HCN)/\rho - k_b(HCN)$$

or

$$\rho/t = k_b\alpha\beta - k_b\rho \tag{3}$$

The k_b and $\alpha\beta$ values in Table 2 were calculated using eq. 3 by determining the slopes and intercepts of plots of ρ/t vs. ρ. An Arrhenius treatment gives the temperature dependence for k_b as

$$k_b = 10^{6.8\pm.6} \exp(-39{,}500 \pm 3{,}400/RT)\,(\text{sec}^{-1}) \tag{4}$$

It is now possible to reexamine the first-order assumption in regards to the decomposition rate of the intermediate. Eq. (1) can be written in terms of a general order, n

$$(HCN)/t = k_b(\beta A)^n \tag{1a}$$

Using eq. 2 for (A) and (HCN) = ρX the following is obtained

$$\rho/t = k_b\beta^n X^{n-1}(\alpha - \rho/\beta)^n \tag{3a}$$

The value of X will increase with an increase in initial concentration of the pyridine unless its decomposition in step (a) were zero order, which it is not. Thus, since ρ was experimentally determined to be constant and all other quantities in eq. (3a) are constants at a given contact time and variable X, n must be one.

It is interesting to note that at the two higher temperatures α and β are essentially one, thus, all of the pyridine appears to be converted to an intermediate which can form HCN if given sufficient time to react. This is not true at 900 ^{o}C where $\alpha\beta$ is only about 0.6.

It is evident, from this and previous studies, that HCN is by far the most abundant nitrogen containing product in the inert pyrolysis of pyridine and other heterocycles, the conversion is essentially quantitative for pyridine at 1100 ^{o}C (4,7). However, the identity of the intermediate species leading to HCN formation is not certain. From the preceeding discussion the fraction of decomposed pyridine which can form HCN is

$$(\beta A/X) = \alpha\beta - \rho \tag{5}$$

These values range from 0.16 to 0.77 using the results in Table 2, which indicates that a significant concentration of intermediate builds up at all conditions. The product yields reported from previous and current studies (4,7,8) show that no volatile nitrogen containing product comes close to that range of yields.

Other possibilities for the intermediate are the heavier molecules such as those in the tarry residue found at the reactor exit. They contain a large fraction of fuel-nitrogen, as indicated by elemental analysis of the residues formed at 950 C(16% N) and 1000 C (10% N) (8). However, since the residue from the reactor, once formed at 950 C, did not yield additional HCN when heated to 1110 C, and measurements of HCN evolution from benzonitrile and quinoline indicated these gave lower yields than did pyridine at high temperatures (4), the species leading to HCN formation must form the less reactive tar on cooling after leaving the reactor. This observation also allows volatile species such as vinyl cyanide to be an intermediate if it continues to react on cooling and its measured concentration does not represent its concentration in the reactor.

Task 2

The reviewer's comments on the "Oxidation of Cyanogen" paper submitted to *Combustion and Flame* were not reasonable criticisms. After a minor revision the paper was sent to *Combustion Science and Technology* where it was accepted.

REFERENCES

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