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FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

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ABSTRACT

A study of the reaction mechanism which leads to NO formation from fuel-nitrogen by determining the rates and mechanisms of pyridine pyrolysis and HCN formation was continued. The emphasis was continued on the determination of the rate of formation of HCN in an inert atmosphere since in previous studies it was found to be the major product containing the nitrogen during pyridine pyrolysis at higher temperatures. Using a picric acid-colorometric method for the analysis of HCN, the ratios of moles HCN produced/mole pyridine consumed have been determined at 900, 950 and 1000°C. Since these ratios increased with reaction time and were independent at initial concentration, the data were consistent with a consecutive reaction mechanism, the second step of which was first-order. The rate constant for this second step is described by

$$k_2 = 10^{11.0} \exp(-63,400/RT) (\mathrm{sec}^{-1})$$

The infrared spectra of the cyanogen oxidation products were further analysed. Evidence for CO as well as CO_2 and N_2O was found but NO and NO_2 were clearly not significant products. Only one absorption, at 1030 cm^{-1}, could not be accounted for by the products listed, the origin of this band is still unknown.

OBJECTIVE AND SCOPE

One of the major scientific problems confronting society today is the reduction and control of air pollution. 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 representative, condensed-ring heterocycles, e.g. quinoline, carbazole, etc. 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. cyanogen, HCN, vinylcyanide, etc., 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, gas chromatographic and infrared spectrophotometric monitoring of products and reactants will be carried out also.

SUMMARY OF PROGRESS

Task 2, which consists of experiments to determine the rate and mechanism of pyrolysis of pyridine and also the rate of formation of HCN in an inert atmosphere, has been about 95% completed. The emphasis during this period has continued on the rate of formation of HCN since it was found in previous studies to be the major nitrogen containing product at higher temperatures. Using the picric acid-colorometric analytical method for HCN, the ratio of moles HCN produced/mole pyridine consumed was determined at 900, 950 and 1000°C. Since the ratio increased with reaction time and was independent of initial pyridine concentration, a two step consecutive reaction mechanism for HCN production was assumed, the second step of which was first-order. This allowed the calculation of the rate constant and activation energy for this second step.

Task 4, which is concerned with the oxidation of CN containing species of the type obtained in the inert pyrolysis of pyridine, was still not reactivated. However, additional examination of the infrared spectra of the reaction products at about 50% reaction indicated significant amounts of CO formed as well as CO_2 and N_2O. In addition, an absorption was found at 1030 cm^{-1} which cannot be due to any of the species that have been identified, all other absorptions have been accounted for by the above products and $(CN)_2$.

DETAILS OF TECHNICAL PROGRESS

Task 2

Work continued on a better definition of the mechanism of pyridine pyrolysis and HCN formation in an inert atmosphere. Assuming that a large fraction of fossil fuels undergo thermal decomposition prior to oxidation and that HCN is the major product containing nitrogen from this pyrolysis, the rate of formation of HCN is of importance to the mechanism under study. Thus, the determination of rate of formation of HCN was continued using the picric acid-colorometric technique previously described (1 f and g).

As discussed in the last report (1g), the time dependence of the ratio, moles HCN formed/moles pyridine decomposed, indicates a consecutive mechanism, the independence of this ratio from variation of initial concentration indicates a first-order second step. The data treatment for consecutive first-order reactions described by Frost and Pearson (2) was tried on the results at 1000°C. A plot of relative concentrations of HCN formed vs pyridine consumed had about the same shape as the theoretical curve for a rate constant ratio of 1.25. However, this treatment is unsatisfactory for two reasons: (a) the first step is not first-order but autocatalytic, and (b) this program uses a stirred-flow reactor but the treatment is for integral data. Because of this it was necessary to develop an equation to treat the differential data.

Using the following scheme and a first-order dependence of step 2, the

$$C_5H_5N \longrightarrow \text{Intermediate (I)} \qquad (1)$$

$$I \longrightarrow HCN + \text{Product} \qquad (2)$$

rate of step 2 is given for a stirred-flow reactor by equation 3 (3)

$$d(HCN)/dt_c = (HCN)/t_c = k_2(I) \qquad (3)$$

If it is assumed that (I) is proportional to the difference between the change in pyridine concentration and the HCN concentration evolved, then

$$k_2 = \rho / t_c(1-\rho) \qquad (4)$$

where ρ is the measured ratio of HCN formed to pyridine consumed and t_c is the contact time. The data and rate constants are summarized in Table 1 (some data are repeated from the last report to be more complete). An Arrhenius treatment of the average values of k_2 give the temperature dependence as

$$k_2 = 10^{11.0 \pm 1.4} \exp(-63{,}400 \pm 7{,}600/RT) \ (\mathrm{sec}^{-1}) \qquad (5)$$

Two points should be noted about the summarized results: (a) the k_2 values have a large scatter, but show no significant trend with concentration or time, and (b) the order of the first step does not figure into the calculation of the second step rate constant. Thus, these data are necessary to allow reasonable extrapolatability of the rate of formation of HCN at higher temperatures. For example, the rate of disappearance of pyridine is described by a first-order and autocatalytic two term rate equation with activation energies of 48 and 112 Kcal respectively (1 b), but the temperature dependence of the rate of formation of HCN is not as large at 950°C and above.

Task 4

Although no new data was obtained during this period on the oxidation of cyanogen, the infrared spectra were examined in more detail and the following is a tabulation of the observations. The reaction conditions wer 1000°C or 1050°C with each reactant initially at 2% in the mixture, the extent of reaction was about 50%. All absorptions appear reasonably accounted for except for that at 1030 cm^{-1}. This is not due to C_3O_2 and

Table 1
RATE OF HCN FORMATION

Initial Concentration (Mole % Pyridine)	Contact Time (sec)	Fraction Reacted (%)	ρ* (HCN/C_5H_5N)	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
				Av .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
				Av .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
				Av 1.13

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*Ratio of moles HCN formed to moles pyridine decomposed.

does not appear to be due to any stable nitrogen or carbon oxide reported (4). The lack of an absorption between 1300 and 2100 cm^{-1} is important to show the absence of NO and NO_2 as well as C=N, N=N (unsymetrical) and C=O type bonds in the products. Two points to be noted about the 1030 absorption: (a) it is spiked with a shoulder on each side indicating a possibility of P-Q-R branches and thus a bending mode, and (b) it is relatively larger at 1050°C than at 1000°C for approximately the same extent of reaction. After the assembly of the quadrupole mass spectrometer, it may be possible to identify this species.

An additional point of concern is the pathway leading to the formation of N_2O. It cannot arise from NO, from molecular nitrogen or from the original $(CN)_2$. It is possible that N atoms from the partial oxidation of $(CN)_2$ could attack the reactant to form a CNN species but this would require double bonds which do not appear in the final products. These studies will continue as soon as possible.

Tasks 1, 3, 5 and 6

The assembly of the mass spectrometer to complete Task 1 is underway; the other tasks will be undertaken at a later date.

Table 2

IR DATA - $(CN)_2$ OXIDATION

Before Reaction	After Reaction	Comments	
(cm^{-1})			
	590	$N_2O-\nu_2$	
	670	$CO_2-\nu_2$	
725 $(CN)_2$	725	$(CN)_2-\nu_2$	decreased to about ½ original size
740 $(CN)_2$	740		
	1030		new & unidentified
	1270	$N_2O-\nu_1$	
	1300		
	2120	CO	
2150 $(CN)_2$	2150	$(CN)_2$ & CO	due to overlap these did not decrease in size
2170 $(CN)_2$	2170	$(CN)_2$ & CO	
	2220	$N_2O-\nu_3$	
	2240		
	2280	$C^{13}O_2-\nu_3$	large increase in size
2330-60 (CO_2 impurity)	2330-60	$CO_2-\nu_3$	
2560 $(CN)_2$	2560	$(CN)_2$	decreased to about ½ original size
2660 $(CN)_2$	2660	$(CN)_2$	

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