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FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

Quarterly Progress Report for the Period
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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 950 and 1000°C. From the results it appears that HCN is formed through a consecutive reaction mechanism, since the ratio increases with reaction time. These studies are being continued.

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. Thus, the rate of formation of this key product is of critical importance. The picric acid-colorometric analytical method for HCN, described in the last quarterly report, has given consistent data at 950 and 1000°C. These results indicate the HCN is formed in a reaction subsequent to the initial disappearance of pyridine, i.e. in the second or later step of a consecutive series. Work will continue on obtaining and interpreting the rate of formation of HCN data.

Task 4, which is concerned with the oxidation of nitrogen-containing intermediate species has been discontinued temporarily. The graduate student that had been working on the project obtained employment in a computer center before this thesis research had been completed and is no longer in the graduate program. Thus, a material balance for the oxidation of cyanogen is still to be determined.

DETAILS OF TECHNICAL PROGRESS

Task 2

Work concentrated on a better definition of the mechanism of pyridine pyrolysis and HCN formation in an inert atmosphere. For the construction of a model for the formation of NO from fuel-nitrogen, it is necessary to obtain data on many facets of the problem. If, for example, fuels pyrolyse to form HCN from the chemically bound nitrogen before oxidizing species can reach these fuels, then the rate of HCN formation, which may be significantly different than the rate of disappearance of fuel, must be determined. Thus, the reason for the current emphasis on HCN formation.

Using the picric acid-colorometric technique described in the previous report (1f), the concentration of HCN in the flow stream was determined. Since the fraction of pyridine reacted was measured chromatographically during the run used for the HCN determination, it was possible to calculate a ratio of moles HCN produced to moles pyridine reacted. These results at 950 and 1000°C are summarized in the table. It should be noted that since the experiments required a complex wet chemical analytical technique, they were quite time consuming.

It can be seen that the ratio generally increases with time and temperature and appears independent of initial concentration. The time dependence would indicate a consecutive mechanism operating, with a significant delay between reactant disappearance and product formation. The rate data will be subjected to a treatment for consecutive reactions and discussed in the next report.

RATE OF HCN FORMATION

Initial Concentration (Mole % Pyridine)	Contact Time (sec)	Fraction Reacted (%)	Ratio* (HCN/C_5H_5N)
950°C			
1.0	0.5	25	.235
2.0	0.5	46	.122
0.5	1.0	31	.412
1.0	1.0	40	.520
2.0	1.0	59	.247
0.5	2.0	46	.553
1.0	2.0	54	.416
2.0	2.0	64	.427
1.0	4.0	70	.593
2.0	4.0	66	.627
1000°C			
0.5	0.5	39	.43
1.0	0.5	50	.33
2.0	0.5	57	.34
0.5	0.5	43	.37
2.0	0.75	66	.47
0.25	1.0	43	.48
0.5	1.0	54	.52
1.0	1.0	63	.52
2.0	1.0	76	.49
2.0	1.0	80	.52
1.7	1.7	84	.64
0.5	2.0	67	.64
1.0	2.0	77	.75
2.0	2.0	76	.73

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*Ratio of moles HCN formed to moles pyridine decomposed.

Tasks 1, 3, 4, 5 and 6

Task 1 will be completed with the assembly of the quadrupole mass spectrometer, which has been postponed because of the other experiments currently being carried out; the other tasks will be undertaken at a later date.

REFERENCES

1. (a) T. Houser, "Fundamentals of Nitric Oxide Formation in Fossil Fuel Combustion," ERDA, FE-2018-1, QPR Period June-Sept. 1975.

   (b) ERDA, FE-2018-2, QPR Period Sept.-Dec. 1975.

   (c) ERDA, FE-2018-3, QPR Period Dec. 1975- Mar. 1976.

   (d) ERDA, FE-2018-4, QPR Period Mar.-June 1976.

   (e) ERDA, FE-2018-5, QPR Period June-Sept. 1976.

   (f) ERDA, FE-2018-6, QPR Period Sept.-Dec. 1976.

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