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FUNDAMENTALS OF NITRIC OXIDE FORMATION IN FOSSIL FUEL COMBUSTION

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ABSTRACT

The quadrupole mass spectrometer was assembled and put into operation. Using this instrument, several spectra of mixtures of reaction products and of pure compounds of interest were produced. These confirmed that acetylene was produced in a much greater yield than methane, that diacetyline and buten-3-yne as well as vinyl cyanide and some acetonitrile are produced, and that the benzene yield is about 4 mole % of the pyridine decomposed. A corrected derivation for the rate constant of the HCN yielding step was also included which modified the Arrhenius equation for this step to

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

where α is the proportionality constant used to describe the concentration of intermediate which converts to HCN.

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 1, which consists of constructing the apparatus to make the experimental determinations described in the other tasks has been completed. The quadrupole mass spectrometer, with special atmospheric sampling probe, was assembled and was used to obtain spectra.

Task 2, which consists of experiments to determine the rate of pyrolysis of pyridine and rate of formation of important nitrogen containing products, specifically HCN in this case, in an inert atmosphere has been about 95% completed. It has been difficult to bring this task to termination because as information is obtained, a need for additional experiments is suggested. The mass spectra of pyridine pyrolysis product mixtures and of pure compounds of significance to the pyrolysis were obtained. These showed conclusively that acetylene was the major light organic molecule produced and is probably the source of the benzene formed and that the benzene was in a yield of about 4 mole % of the pyridine decomposed. The mass spectra indicated that as well as the vinyl cyanide, previously reported, amounts of diacetylene, buten-3-yne and acetonitrile (in about equal yields of the order of one mole %) were found.

DETAILS OF TECHNICAL PROGRESS

Task 1

The quadrupole mass spectrometer has been assembled and made operational. Its components consist of:(a) high-speed, high-vacuum, mechanical and oil diffusion pumps for the vacuum system (pressures below 10^{-7}Torr have been obtained), (b) a special probe chamber with a micrometer needle valve and heated capillary for the sample inlet to obtain samples at atmospheric pressure, (c) an RF generator, and (d) a control console. All components, excluding the two mechanical pumps, were mounted on a wheeled cart for mobility and positioning purposes. This new unit, UTI-100C, gives improved sensitivity, resolution and mass range, 2-400 amu, over the previously used MS-10. This assembly completes Task 1.

Task 2

The quadrupole mass spectrometer assembled in Task 1 was used to examine the decomposition products of pyridine, the rate of which had been reported previously (1 a-h). Since each instrument will vary somewhat with respect to the cracking pattern for a given compound, several known species of interest to the pyrolysis were examined also. The results of the known compounds are listed in Table 1 as relative ion currents (per cent of the most abundant ion). These compounds were introduced through the flow system and atmospheric sampling probe to simulate experimental conditions. The spectra are in reasonable agreement with those reported in the literature for these compounds (2).

Mass spectra of the flow stream at the reactor inlet and exit were obtained also. The results of two typical experiments are given in Table 2,

Table 1

RELATIVE ION CURRENTS OF KNOWN COMPOUNDS

m/e	CH_4	C_2H_2	CH_3CN	CH_2CHCN	C_6H_6	C_5H_5N
80						4.9
79					6.4	81
78					100	9.8
77					24.4	-
53				68	1.4	10.1
52				61	30	100
51				26.0	32	48
50				6.7	30	37
49				-	3.5	7.1
48				-	-	0.9
41			100	-	-	0.7
40			52	-	-	-
39			20.7	2.2	21.1	14.7
38			13.4	6.1	7.4	7.0
37			-	4.5	4.3	4.8
27		1.7	5.8	22.1	6.8	9.5
26		100	5.6	100	6.4	24.5
25		21.7	2.9	10.3	-	2.4
24		6.0	1.3	3.1	-	-
16	100	-	-	-	-	1.6
15	77	-	2.0	-	-	-
14	11.4	-	11.6	1.1	-	-
2	-	-	-	2.8	3.5	4.9

Table 2

ION CURRENTS[a] FROM PYRIDINE PYROLYSIS

Reaction Conditions[b]				
C_o (mole %)	1		2	
t_c (sec)	2		4	
temp. (°C)	1000		1070	
F	.87		.97	
m/e	Entrance	Exit	Entrance	Exit
79	4.41	.56	7.50	.24
78	.53	.22	.89	.28
77	-	-	.04	.07
53	.62	.12	.92	.05
52	5.81	.82	9.10	.41
51	2.69	.58	4.33	.29
50	2.07	.45	3.34	.25
49	-	-	.65	.05
48	-	-	.08	.01
41	.06	.08	.06	.06
39	.86	.18	1.34	.13
38	-	-	.64	.06
37	-	-	.44	.04
27	.50	2.74	.86	8.70
26	1.44	5.69	2.23	7.60
25	.15	1.18	.22	1.33
24	.02	.35	.03	.39
16	.14	.44	.15	.74
15	.03	.23	.03	.46
14	.06	.12	.02	.19
2	0	1.20	.45	4.35

[a] Times 10^7 amp.

[b] C_o is initial pyridine concentration, t_c is contact time, F is fraction reacted.

all ion currents reported are above background. The very large extents of reaction were used to reduce the ion fragments from pyridine. Inspection of the data in the tables quickly gives qualitative and semiquantitative information. The following conclusions have been drawn:

a. Hydrogen is a significant product.

b. Some methane is produced, but the amount is much less than acetylene which is shown by comparing ion currents at masses 26 and 25 with those at 16 and 15, (although some of the 26 is due to HCN, its contribution would be small, and none of the 25 comes from HCN).

c. Benzene is a significant product at about 4 mole % of the total pyridine decomposed.

d. Although the information is not as clear in the mass range of 53 to 49, these ion currents are larger than would be predicted from pyridine and benzene alone, and could be accounted for by the presence of vinyl cyanide, buten-3-yne and diacetylene in approximately equal molar amounts.

e. The 41 ion indicates some acetonitrile formed but probably less than the diacetylene and vinyl cyanide.

f. The relative amounts of H_2 and HCN produced increase as the temperature increases, the HCN increase agrees with the previously reported work (1 h).

A comparison of these conclusions with those reported by Axworthy, et.al. (3) is worthwhile. They have reported a very large fraction of product in the form of methane and no acetylene was formed. This is clearly contrary to our observations. In addition, what they have reported as acetonitrile from chromatographic measurements, appears to be a mixture of mainly diacetylene, some acetonitrile and possibly buten-3-yne.

Attempts to be more quantitative about these mass spectral data will be made later.

The following is a corrected derivation of the rate constant for the reaction leading to HCN formation, which was erroneously reported in the previous report (1h). The k_2 in eq (3) was not the same as the k_2 in eq (4).

Again starting with the 1st-order rate of the step yielding HCN and using stirred-flow kinetics (4)

$$d(HCN)/dt_c = (HCN)/t_c = k_2(I)$$

Assuming that the intermediate concentration, (I), is proportional to (α is the proportionality constant) the difference between the change in pyridine concentration and the HCN concentration evolved, then

$$(I) = \alpha[\Delta P - (HCN)]$$

and if ρ = (HCN)/ΔP (moles HCN produced per mole pyridine consumed), the rate equation can be rewritten

$$\text{rate} = (HCN)/t_c = k_2\alpha[(HCN)/\rho - (HCN)]$$

or $$k_2\alpha = \rho/t_c(1-\rho)$$

The Arrhenius treatment gives the temperature dependence for the product $k_2\alpha$

$$k_2\alpha = 10^{11.0\pm1.4}\exp(-63{,}400 \pm 7{,}600/RT)(sec^{-1})$$

Tasks 3, 4, 5, and 6

There is no progress to report on these tasks during this period.

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.

   (g) ERDA, FE-2018-7, QPR Period Dec. 1976-Mar. 1977.

   (h) ERDA, FE-2018-8, QPR Period Mar.-June 1977.

2. "Index of Mass Spectral Data," American Society for Testing and Materials, (1969).

3. A.E. Axworthy, G. R. Schneider, M.D. Shuman and V. H. Dayan, "Chemistry of Fuel Nitrogen Conversion to Nitrogen Oxides in Combustion," EPA-600/2-76-039, Feb. 1976.

4. K.J. Laidler, "Chemical Kinetics," McGraw-Hill, Inc., New York, 1965, pp 21-24.