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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 stuctures. 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. The study of the oxidation kinetics of pyridine was completed in the temperature range of 948 to 1073 K and concentration ranges of 1.75 to 7.0 mole % oxygen; 0.25 to 2.0 mole % pyridine. The rate law that best describes the data is:

$$\text{rate} = k(C_5H_5N)^{1/2}(O_2)(\Delta O_2)^{1/2}$$

The (ΔO_2) factor (concentration of oxygen consumed) is necessary to keep the data from stratifying according to initial oxygen concentrations and indicates autocatalysis is occurring. The temperature dependence of the rate constants obtained from this equation is expressed by

$$k = 10^{14.7 \pm .7} \exp(-26600 \pm 1600/T)\,(\text{l/mole sec})$$

An examination of the volatile nitrogen containing oxidation products indicated that at these conditions the yield of HCN (about 40 to 60% of the reacted pyridine) appeared insensitive to changes in temperature, concentrations and equivalence ratio, and only trace amounts of nitrogen oxides and ammonia were found. Fuel rich mixtures produced large amounts of smoke so that a nitrogen balance was not possible but for lean mixtures HCN and N_2 accounted for the product nitrogen, within a large experimental uncertainty. An increase in the concentrations of reactants to 2% pyridine and 14% oxygen produced a significant change in the products with yields of HCN reduced and those of N_2, N_2O and NO increased. These observations clearly indicate a shift in mechanism as the concentrations increase. A few experiments were run to determine the influence of H_2 on the rates of pyrolysis and oxidation of pyridine; the results showed no influence.

Task 2. The study of the rate and products of oxidation of HCN at lower temperatures was initiated. At 1073 it was found that: (a) HCN was oxidized at a measurable rate, (b) added benzene increased the rate of oxidation at low equivalence ratios and reduced it at ~~ratios~~ above 0.9, with no significant nitrogen oxides produced, (c) added acetylene increased the oxidation rate and also produced NO.

Mechanism Discussion. From the above results and those reported earlier it is clear that conditions can be found for the oxidation of heterocyclic nitrogen compounds that promote the formation of N_2 at the expense of NO. These conditions relate to both concentration and temperature and work will continue to better define them.

DETAILS OF TECHNICAL PROGRESS

Task 1

Task 1 which consists of the study of the oxidation of pyridine, was continued with the completion of the experiments that determined the rate of oxidation in the temperature range of 948 to 1073 K. A complete summary of the data is given in Table 1 including the results from 1979 (1) and those from 1980 reported previously (2). The experiments were repeated primarily to measure the formation of HCN over a wide range of conditions and of NO, NH_3 and N_2 over a more limited set of conditions. Thus, all experiments reporting HCN yields, and only those, are from the current year.

In addition, when the previous results were reexamined, an error in the flow calibrations for the He/O_2 mixtures was discovered. Correction of the flow rates resulted in slightly different reaction times, rates and initial concentrations of pyridine in Table 1 than those reported earlier (1).

The rate equation reported previously (3) still gave the best description of the data over a wide range of fuel rich to lean ratios

$$\text{rate} = k(C_5H_5N)^{\frac{1}{2}}(O_2)(\Delta O_2)^{\frac{1}{2}} \qquad (1)$$

where (ΔO_2) is the oxygen consumed and indicates autocatalysis. Figures 1-6 illustrate the data plotted as rate vs the concentration function in equation (1) at each temperature. It is believed that the intercepts are about zero, within the uncertainties of the data, thus the k values in Table 1 were computed with this assumption and the averages reported with the standard deviation of the mean and the standard deviation of the points, σ. These rate constants yield an activation energy for the oxidation of pyridine of 52.8 $\pm$ 3.2 K cal/mole and log A of 14.7 $\pm$ .7.

An examination of the HCN yields indicates that there appears to be no significant trend with any of the variables, time, temperature or concentrations,

Table 1

Data Summary*

Co (mole %) $(C_5H_5N)/(O_2)$	time (sec)	%HCN	Fraction Reacted (%) C_5H_5N	O_2	Rate x 10^5 (mole/l·sec)	CF x 10^7	k (l/mole·sec)
			948 °K				
1.1/1.75	4.4		11	15	.351	.1167	301
1.1/1.75	8.4		26	60	.415	.0982	423
2.1/1.75	8.3		10	79	.319	.0903	353
.27/3.5	2.1		33	10	.527	.1241	425
.28/3.5	4.4		72	21	.575	.1035	556
.56/3.5	4.4		59	33	.941	.1873	502
1.1/3.5	4.4		30	36	.958	.3415	280
2.0/3.5	4.0	(18)	39	31	2.439	.4215	578
1.0/3.5	2.0	(51)	10	7	.625	.2355	265
2.0/3.5	2.0	(44)	10	14	1.251	.4292	291
1.0/3.5	4.0	(58)	24	19	.751	.3108	241
.28/7.0	2.2		60	11	.958	.2868	334
.56/7.0	2.2		55	17	1.756	.4959	354
.56/7.0	4.4		82	29	1.309	.3487	375
1.1/7.0	4.4		69	47	2.202	.6082	362
1.1/7.0	2.2		49	34	2.982	.8152	366
2.2/7.0	4.4		66	40	4.213	.9285	454
2.2/7.0	2.2		40	31	5.107	1.2487	409
1.0/7.0	2.0	(39)	55	24	3.429	.7117	482
2.0/7.0	2.0	(43)	22	21	2.752	1.2714	216
2.0/7.0	4.0	(65)	51	55	3.190	.9281	344
.28/7.0	4.4		80	19	.638	.2414	264
						Average	372 ± 21
						σ = 99	

Co (mole %) $(C_5H_5N)/(O_2)$	time (sec)	%HCN	Fraction Reacted (%) C_5H_5N	O_2	Rate x 10^5 (mole/l·sec)	CF x 10^7	k (l/mole·sec)
			973 °K				
1.1/1.0	4.3		6	5	.1834	.0311	590
2.1/1.0	4.2		8	43	.4890	.0749	653
1.1/1.0	9.2		18	63	.2742	.0416	659
2.3/1.0	9.1		17	68	.5196	.0521	997
0.58/1.0	9.3		29	57	.2212	.0307	721
1.1/1.0	9.2		31	54	.4722	.0440	1073
1.1/1.75	4.2		28	45	.8557	.1066	803
0.53/1.75	4.3		28	30	.4265	.0811	526
0.50/1.75	4.0	(48)	42	30	.6400	.0705	908
1.0/1.75	4.0	(55)	20	30	.6090	.1162	524
0.27/1.75	4.3		44	24	.3356	.0494	679
1.1/1.75	2.1		18	23	1.1002	.1174	937
0.58/1.75	9.2		46	64	.3509	.0549	639
2.1/1.75	4.2		23	51	1.4059	.1486	946
2.0/1.75	2.0	(20)	11	16	1.3400	.1495	896
2.0/1.75	4.0	(32)	21	40	1.2794	.1592	804
0.27/3.5	2.2		42	13	.6398	.1204	531
0.27/3.5	4.4		70	25	.5340	.1041	513
0.58/3.5	1.2		15	9	.9169	.1849	496
0.25/3.5	2.0	(52)	51	16	.7721	.1140	682
.42/3.5	4.4		50	39	.5746	.1687	341

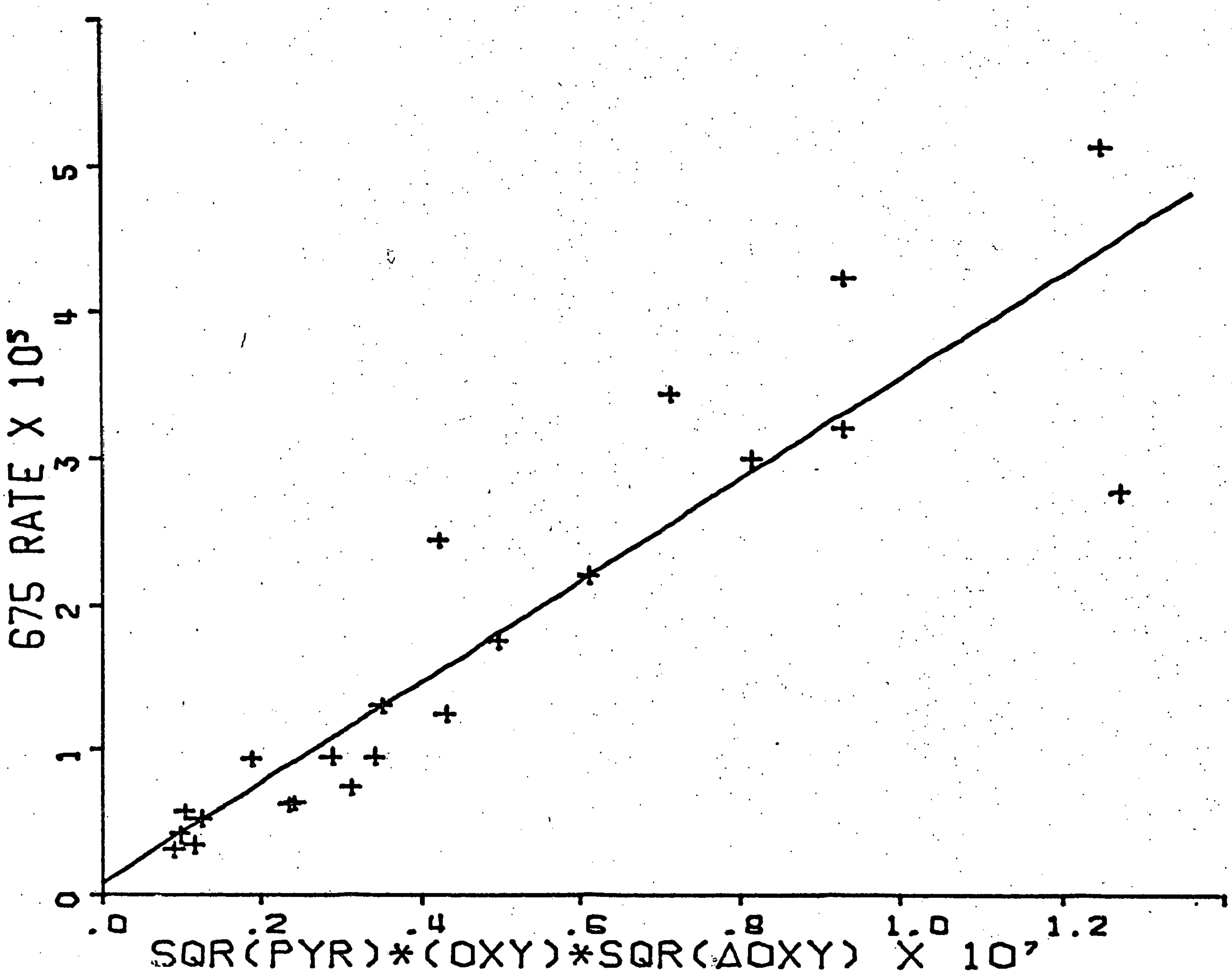
Co (mole %) $(C_5H_5N)/(O_2)$	time (sec)	%HCN	Fraction Reacted(%) C_5H_5N	O_2	Rate x 10^5 (mole/l·sec)	CF x 10^7	k (l/mole sec)
			973 °K (cont'd)				
1.1/3.5	1.1		12	15	1.4641	.3168	462
1.1/3.5	4.4		50	48	1.5281	.2566	596
1.1/3.5	2.1		32	30	1.9560	.3139	623
1.0/3.5	2.0	(64)	23	21	1.4012	.3044	460
2.0/3.5	2.0	(31)	27	26	3.2892	.4301	765
2.3/3.5	1.1		11	14	2.6814	.4282	626
2.1/3.5	2.1		22	33	2.6841	.4668	575
0.59/7.0	1.2		31	9	1.8959	.4735	400
0.55/7.0	2.2		50	23	1.5281	.5267	290
0.56/7.0	4.4		76	34	1.1577	.3834	302
0.25/7.0	0.5	(41)	41	7	2.4978	.2591	964
0.25/7.0	2.0	(47)	78	16	1.1885	.2161	550
0.5/7.0	0.5	(34)	39	11	4.7510	.4451	1067
0.5/7.0	1.0	(50)	54	13	3.2898	.4107	801
0.5/7.0	2.0	(59)	76	24	2.3141	.3521	657
0.66/7.0	5.3	(46)	85	46	1.2951	.3148	411
1.2/7.0	1.2		22	13	2.6841	.8079	332
1.1/7.0	2.2		45	26	2.7506	.7896	348
1.1/7.0	4.4		72	51	2.2005	.5274	417
1.0/7.0	2.0	(56)	70	36	4.2646	.5701	748
2.3/7.0	1.2		19	18	4.6315	1.2734	364
2.2/7.0	2.2		40	41	4.8802	1.1468	426
2.2/7.0	4.4		49	68	2.9951	.7426	403
2.0/7.0	1.0	(36)	39	25	9.5030	1.1057	859
2.0/7.0	2.0	(53)	54	46	6.5783	.9373	702
2.2/7.0	4.4	(62)	66	70	4.0209	.5760	698
						Average	633 ± 31
						σ =	213
			998 °K				
.27/1.0	2.1		28	21	.425	.0223	1906
.53/1.0	2.1		13	21	.396	.0345	1148
.54/1.0	4.2		39	46	.591	.0295	2003
1.1/1.0	4.2		31	59	.943	.0378	2495
1.2/1.0	9.2		30	71	.455	.0307	1482
2.2/1.0	4.3		26	60	1.576	.0537	2935
1.0/1.75	1.0	(38)	11	8	1.303	.0789	1651
0.5/1.75	2.0	(56)	33	25	.978	.0703	1391
2.0/1.75	2.0	(24)	23	34	2.724	.1512	1802
1.1/1.75	2.1		32	45	1.939	.1016	1908
1.1/1.75	1.1		19	20	2.303	.1083	2127
2.1/1.75	2.1		29	54	3.515	.1316	2671
0.5/3.5	0.5	(43)	22	8	2.606	.1489	1750
1.0/3.5	1.0	(46)	30	24	3.554	.2833	1255
1.0/3.5	2.0	(58)	43	47	2.548	.2497	1020
2.0/3.5	4.0	(49)	44	65	2.607	.2674	975
.52/3.5	0.5		39	17	4.727	.1770	2671

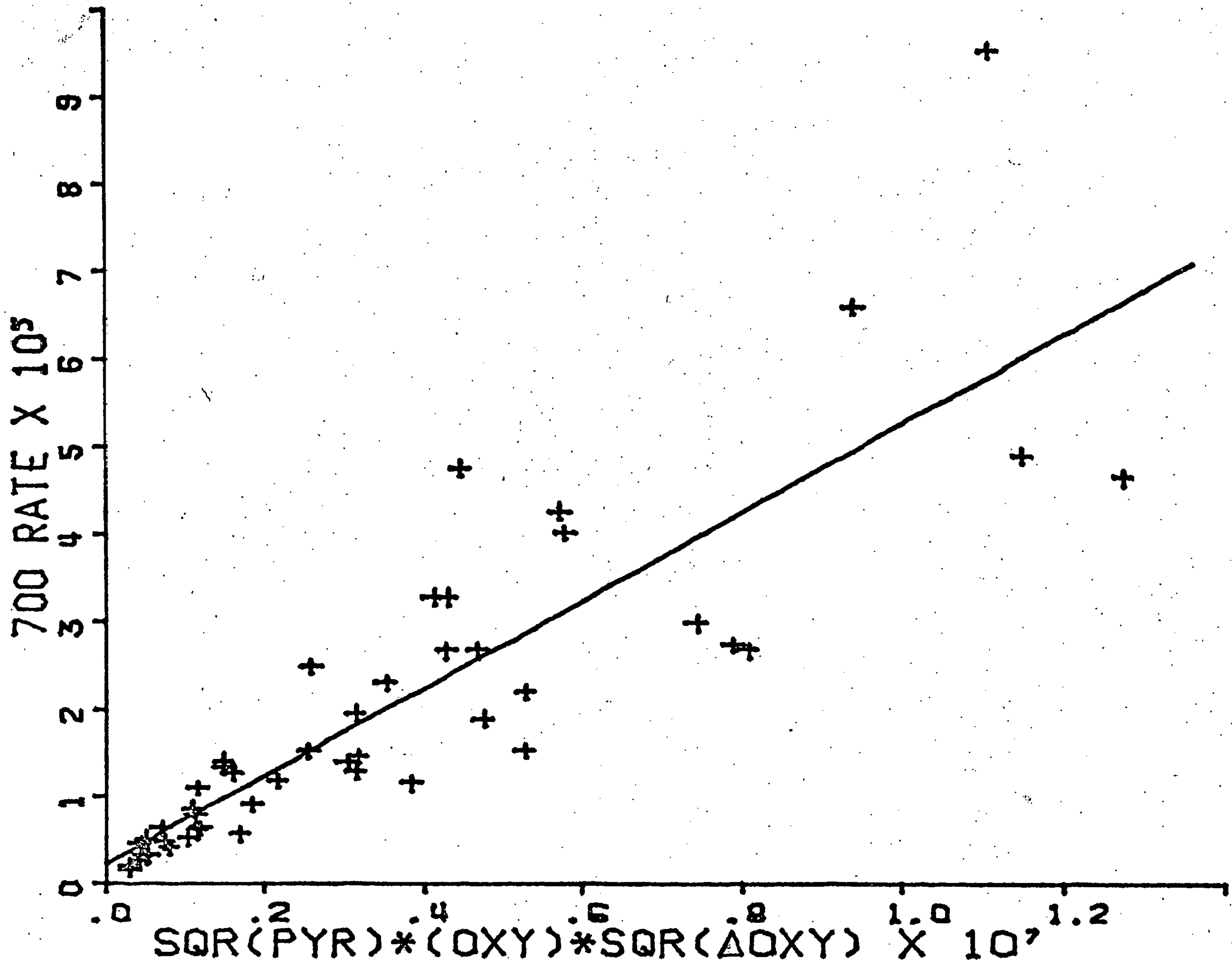
Co (mole %) $(C_5H_5N)/(O_2)$	time (sec)	%HCN	Fraction Reacted (%) C_5H_5N	O_2	Rate x 10^5 (mole/l·sec)	CF x 10^7	k (l/mole sec)
			998 °K (cont'd)				
.54/3.5	1.1		40	24	2.424	.1947	1245
1.0/3.5	2.1		57	53	3.454	.2119	1630
1.1/3.5	1.1		28	25	3.394	.3019	1124
2.2/3.5	2.1		39	58	4.727	.3296	1434
2.2/3.5	4.4		49	79	2.969	.1775	1673
.5/7.0	0.5	(35)	65	16	7.700	.3642	2114
2.0/7.0	0.5	(41)	27	17	12.793	1.0475	1221
1.0/7.0	0.5	(45)	47	20	11.135	.6701	1662
2.0/7.0	2.0	(41)	70	61	8.292	.5974	1388
.27/7.0	1.1		79	15	2.356	.2052	1148
.52/7.0	0.52		51	15	6.060	.4316	1404
.54/7.0	1.1		71	25	4.218	.3856	1094
1.0/7.0	0.51		44	26	10.665	.7436	1434
1.1/7.0	2.1		76	52	4.515	.4529	997
1.1/7.0	1.1		54	30	6.417	.6979	919
2.2/7.0	2.2		67	64	7.961	.6174	1289
						Average	1605 ± 92
							σ = 530
			1023 °K				
.27/1.0	2.1		40	34	.580	.0206	2816
.28/1.0	1.1		31	18	.902	.0203	4443
.54/1.0	2.1		31	44	.902	.0301	3000
.54/1.0	4.3		46	63	.667	.0211	3161
.55/1.0	1.1		25	28	1.449	.0325	4458
1.1/1.0	8.4		45	79	.652	.0188	3468
1.1/1.0	2.1		20	48	1.159	.0441	2628
1.1/1.0	4.3		29	69	.844	.0301	2804
2.2/1.0	4.3		14	72	.811	.0422	1922
.27/1.75	2.1		60	32	.873	.0389	2244
.28/1.75	1.1		40	24	1.164	.0469	2482
.54/1.75	2.1		45	48	1.309	.0604	2167
.54/1.75	4.3		64	65	.928	.0384	2417
.55/1.75	1.1		30	23	1.738	.0705	2465
1.1/1.75	2.1		42	59	2.434	.0760	3203
1.1/1.75	1.1		25	32	2.897	.1067	2715
1.1/1.75	4.4		48	73	1.397	.0534	2616
2.2/1.75	1.1		19	40	4.404	.1520	2897
1.0/1.75	2.0	(45)	43	43	2.492	.0865	2881
2.0/1.75	1.0	(40)	18	30	4.173	.1482	2816
.25/3.5	.5	(61)	57	18	3.303	.1000	3303
.5/3.5	.5	(50)	52	20	6.029	.1531	3938
.5/3.5	2.0	(49)	80	54	2.318	.0934	2471
1.0/3.5	2.0	(69)	65	59	3.767	.1615	2333
1.0/3.5	1.0	(54)	51	44	5.913	.2254	2623
1.0/3.5	.5	(46)	36	23	8.346	.2561	3259

Co (mole %) $(C_5H_5N)/(O_2)$	time (sec)	%HCN	Fraction Reacted(%) C_5H_5N	O_2	Rate x 10^5 (mole/l·sec)	CF x 10^7	k (l/mole sec)
			1023 °K (Cont'd)				
2.0/3.5	.5	(39)	21	23	9.525	.3923	2428
2.0/3.5	2.0	(48)	48	66	5.565	.2404	2315
.28/3.5	.55		54	14	3.129	.1007	3107
.40/3.5	1.6		71	22	2.066	.1093	1890
.55/3.5	2.2		78	49	2.269	.1081	2099
.55/3.5	1.1		49	28	2.839	.1761	1612
.55/3.5	.55		35	17	4.056	.1791	2265
1.1/3.5	2.2		66	61	3.824	.1608	2378
1.1/3.5	1.1		43	38	4.983	.2620	1902
1.1/3.5	.55		26	22	6.026	.2864	2104
2.2/3.5	2.2		53	69	6.142	.2212	2777
2.2/3.5	1.1		23	45	5.333	.4086	1305
2.2/3.5	.55		19	27	8.812	.4320	2040
.56/6.6	.28		44	11	10.199	.3762	2711
1.1/6.6	.28		42	18	19.480	.6312	3086
.28/7.0	.28		67	9	7.765	.2060	3769
1.1/7.0	2.3		85	65	4.925	.2842	1733
1.1/7.0	.56		52	33	12.053	.6952	1734
2.2/7.0	.28		32	24	29.684	1.1070	2681
2.3/7.0	.56		46	41	21.335	1.0060	2121
2.0/7.0	.5	(65)	65	50	29.483	.7071	4170
1.0/7.0	.5	(56)	79	42	18.316	.4223	4338
						Average	2710 ± 107
							σ = 740
			1048 °K				
.27/1.0	2.2		44	46	.623	.0182	3423
.54/1.0	4.3		41	65	.580	.0202	2871
.54/1.0	2.2		29	48	.822	.0284	2894
1.1/1.0	4.3		22	71	.624	.0282	2212
1.1/1.0	2.2		29	58	1.638	.0353	4640
0.5/1.75	0.5	(53)	35	21	3.960	.0607	6524
.5/1.75	1.0	(60)	50	35	2.829	.0566	4998
1.0/1.75	2.0	(47)	48	56	2.716	.0693	3919
0.5/1.75	2.0	(61)	56	51	1.584	.0483	3280
2.0/1.75	2.0	(16)	35	63	3.960	.0963	4112
.27/1.75	2.2		76	55	1.076	.0251	4287
.27/1.75	1.1		56	34	1.588	.0395	4020
.54/1.75	2.1		63	62	1.787	.0393	4547
.54/1.75	1.1		42	40	2.372	.0627	3783
1.1/1.75	2.1		43	69	2.429	.0586	4145
1.1/1.75	1.1		18	52	2.038	.0955	2134
2.1/1.75	2.1		40	74	4.567	.0726	6291
.25/3.5	0.5	(77)	64	23	3.621	.0925	3915
2.0/3.5	0.5	(40)	36	42	16.293	.3459	4710
1.0/3.5	0.5	(56)	47	38	10.637	.2300	4625
2.0/3.5	2.0	(59)	46	72	5.205	.2009	2591
.28/3.5	1.1		80	32	2.269	.0756	3001
.28/3.5	0.56		60	17	3.389	.0952	3560
.55/3.5	1.1		72	47	4.067	.1187	3426

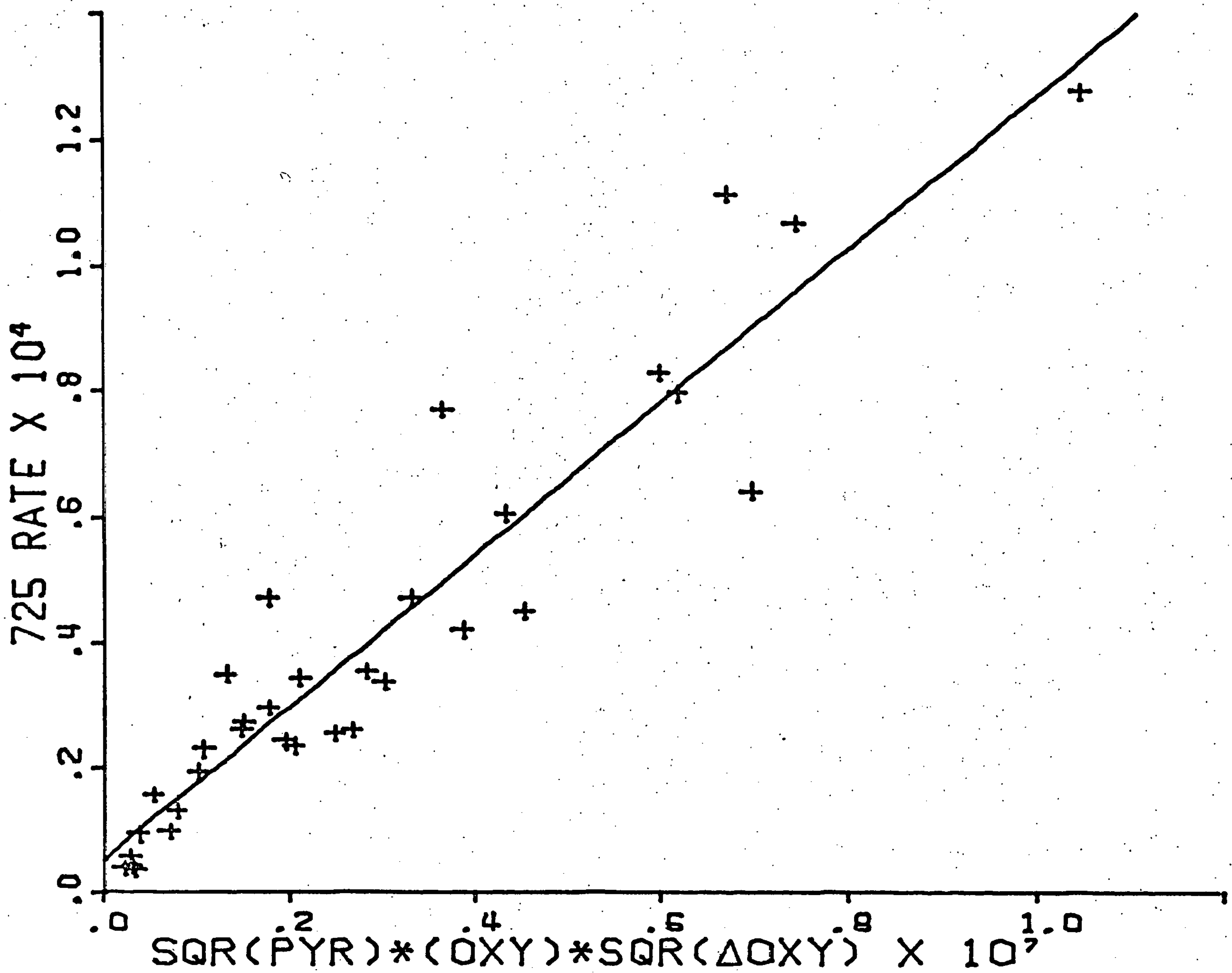
Co (mole %) $(C_5H_5N)/(O_2)$	time (sec)	%HCN	Fraction Reacted(%) C_5H_5N	O_2	Rate x 10^5 (mole/l·sec)	CF x 10^7	k (l/mole sec)
			1048 °K (cont'd)				
.56/3.5	0.55		52	27	5.887	.1632	3607
1.1/3.5	2.2		65	71	3.671	.1245	2949
1.1/3.5	1.1		55	54	6.226	.1964	3170
1.1/3.5	0.55		36	35	8.151	.2672	3051
2.2/3.5	2.2		37	81	4.189	.1619	2587
2.2/3.5	1.1		44	65	9.962	.2543	3917
1.0/7.0	0.44	(58)	83	42	18.784	.3382	5554
2.0/7.0	0.5	(54)	73	63	33.039	.4965	6654
1.0/7.0	0.5	(59)	87	51	19.689	.2947	6681
.29/7.0	0.57		94	22	5.309	.1130	4698
.56/7.0	0.28		79	26	17.886	.3049	5866
1.1/7.0	0.57		81	50	18.339	.3836	4781
1.1/7.0	1.1		84	64	9.509	.2867	3317
2.3/7.0	0.57		59	57	26.701	.7188	3715
2.3/7.0	1.1		67	75	15.169	.4302	3526
						Average	4050 ± 190
						σ =	1200
			1073 °K				
.5/1.75	.25	(46)	35	11	7.737	.0472	16390
1.0/1.75	.5	(53)	35	37	7.737	.0861	8990
2.0/1.75	.56	(54)	37	54	16.359	.1102	14840
2.0/1.75	1.0	(51)	31	55	6.852	.1075	6370
.5/1.75	1.0	(61)	69	49	3.813	.0395	9650
1.0/1.75	1.0	(57)	51	57	5.637	.0633	8910
1.0/1.75	2.0	(63)	55	66	3.031	.0515	5890
2.0/1.75	2.0	(57)	37	71	4.088	.0752	5440
.25/3.5	.25	(58)	75	19	8.289	.0703	11790
.5/3.5	.25	(54)	67	28	14.810	.1229	12050
1.0/3.5	.25	(41)	50	38	22.105	.2129	10380
.5/3.5	.5	(52)	88	46	9.726	.0712	13660
1.0/3.5	.5	(56)	70	53	15.473	.1477	10480
2.0/3.5	.5	(59)	54	63	23.876	.2186	10920
2.0/3.5	1.0	(51)	65	76	14.368	.1358	10580
1.0/3.5	1.0	(62)	81	69	8.952	.0885	10120
2.0/7.0	.5	(78)	86	76	38.020	.2430	15650
						Average	10710 ± 770
						σ =	3190

*Co is the initial concentration, %HCN is the fraction of reacted pyridine forming HCN, rate is for the consumption of pyridine, CF is the best concentration function to fit the data, $(C_5H_5N)^{\frac{1}{2}}(O_2)(\Delta O_2)^{\frac{1}{2}}$ and k is the apparent rate constant, Rate/CF.

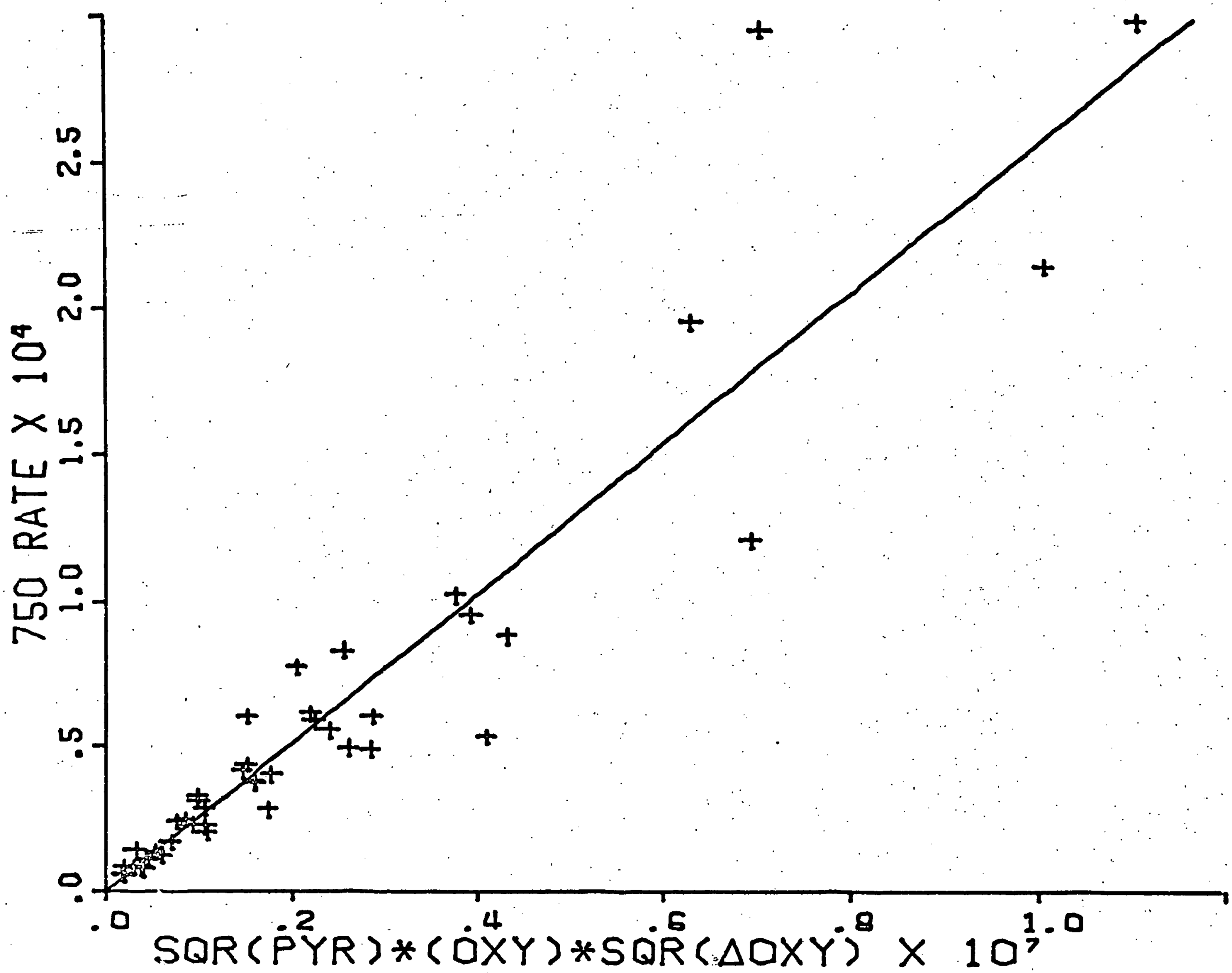

675 RATE X 10⁵
0
1
2
3
4
5
.0
.2
.4
.6
.8
1.0
1.2
SQR(PYR)*(OXY)*SQR(ΔOXY) X 10⁷

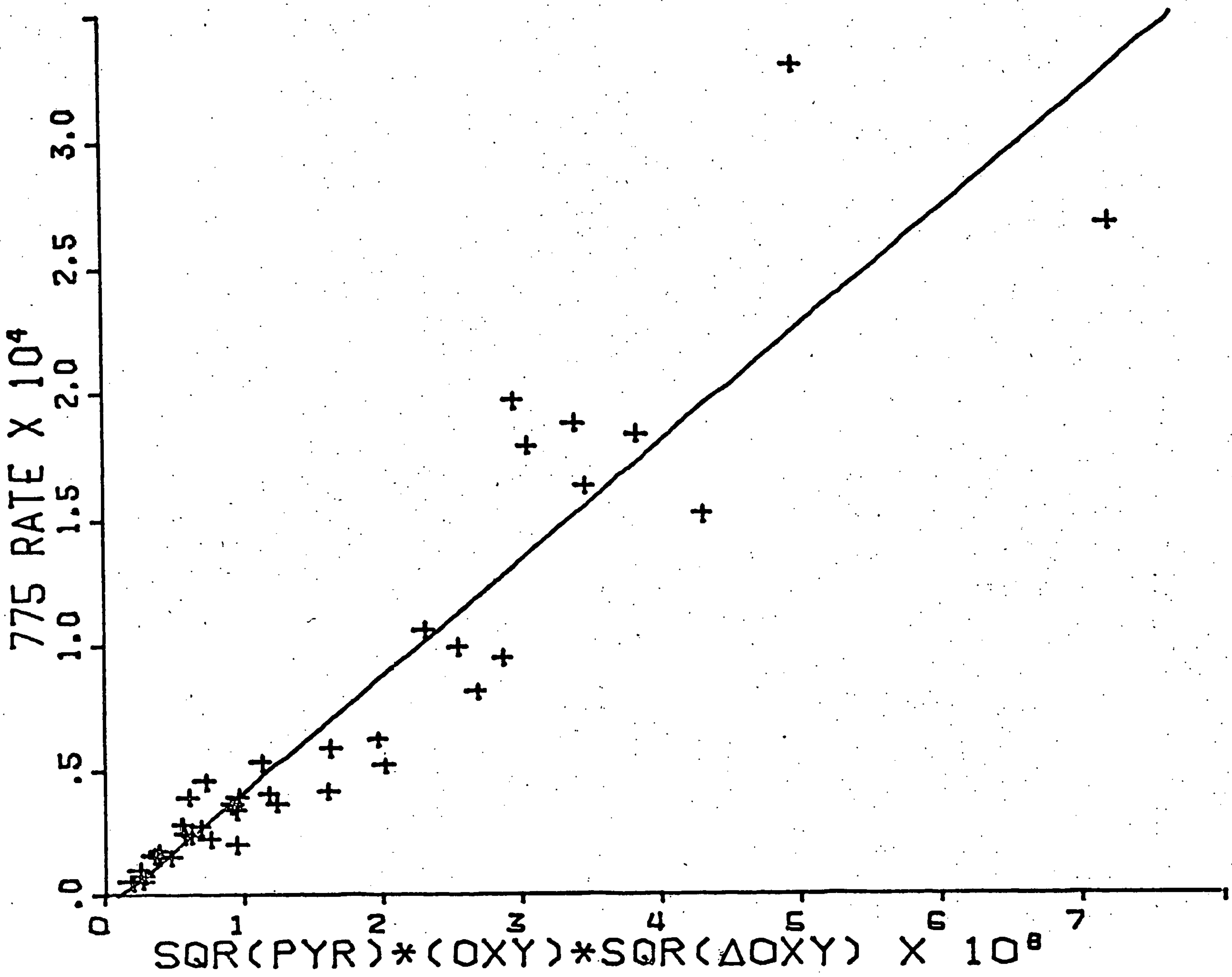


700 RATE X 10⁵
0
1
2
3
4
5
6
7
8
9
.0
.2
.4
.6
.8
1.0
1.2
SQR(PYR)*(OXY)*SQR(ΔOXY) X 10⁷

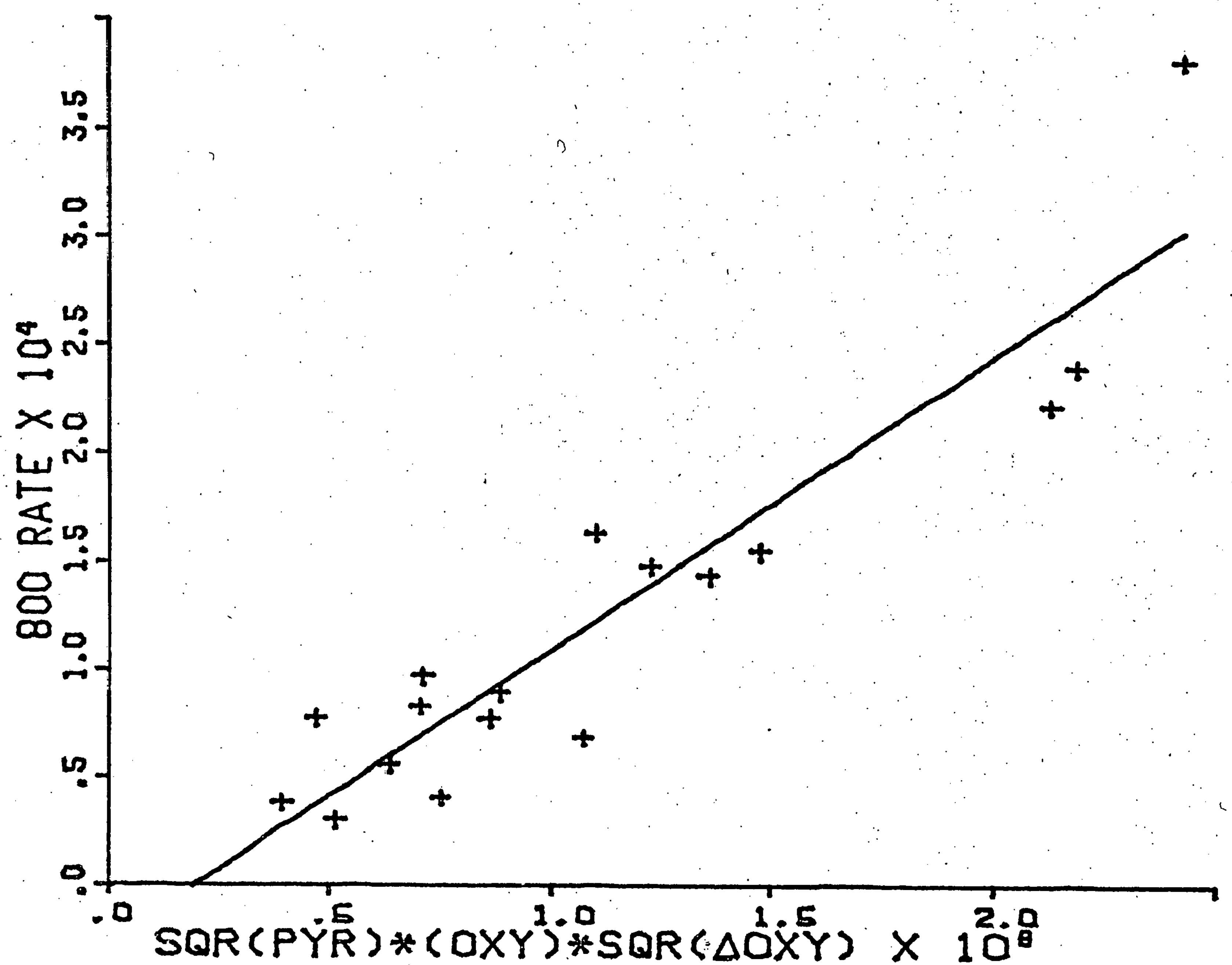


725 RATE X 10⁴
.0
.2
.4
.6
.8
1.0
1.2
.0
.2
.4
.6
.8
1.0
SQR(PYR)*(OXY)*SQR(ΔOXY) X 10⁷


750 RATE X 10⁴
.0
.5
1.0
1.5
2.0
2.5
.0
.2
.4
.6
.8
1.0
SQR(PYR)*(OXY)*SQR(ΔOXY) X 10⁷



775 RATE X 10⁴
0.0
.5
1.0
1.5
2.0
2.5
3.0
0
1
2
3
4
5
6
7
SQR(PYR)*(OXY)*SQR(ΔOXY) X 10⁸



800 RATE X 10^4
.0
.5
1.0
1.5
2.0
2.5
3.0
3.5
SQR(PYR)*(OXY)*SQR(ΔOXY) X 10^8

with the exception that at very fuel rich conditions (2% pyridine, 1.75% oxygen) the yield of HCN was consistently lower. The lack of sensitivity to experimental conditions may indicate HCN is also being oxidized, this possibility is being investigated. The HCN was the only significant volatile, nitrogen-containing product observed for both fuel rich and lean mixtures. Only trace and irregular amounts of nitrogen oxides and ammonia were found.

In order to determine in what form the unaccounted for nitrogen finally evolves under fuel lean conditions, gas chromatographic experiments were initiated with a molecular sieve 5A column to measure molecular nitrogen. Fuel rich conditions produce a large amount of smoke containing nitrogen which does not permit quantitative trapping or measurement. When 0.5 or 1% pyridine with 7% oxygen concentrations were used the uncertainty in the measurements of N_2 was large. However, a few experiments at 1048 and 1073 K indicated that the remainder of the nitrogen was in the form of N_2, within experimental uncertainty, although some N_2O was found at 1073 K. It was decided to increase the concentrations of reactants to 2% pyridine 14% oxygen to improve analytical precision. The results of these higher concentration epxeriments were unexpected.

Only five experiments were run in the 1023 to 1073 K range, all at 2 sec contact time so that the pyridine was completely consumed. In this temperature range very little HCN remained but essentially all the nitrogen could be accounted for, within experimental uncertainty, by N_2 and small, but significant amounts of NO and N_2O. In addition, the mass spectrometer gave rapidly oscillating ion currents for the 14, 28 and 32 ions, indicating that possibly a non-steady state existed in the reactor. These results are more in agreement with those of Axworthy and Dayan (4) who reported large amounts of N_2O and some NO in the 973 to 1073 K range using 75% oxygen.

Because of the mechanisms for pyridine oxidation and pyrolysis that the research group at Purdue have devised, we were requested by Charles Proctor to run a few experiments in our flow system with added hydrogen to examine its effect on these reactions. Their shock tube apparatus had been disassembled. Table 2 summarizes these results. It can be seen that very little, if any, effect is produced by the hydrogen.

Table 2

Effect of Added H_2 (¼ mole%)

Temperature (C)	Time (sec)	Co(mole %) $(C_5H_5N)/(O_2)$	Fraction C_5H_5N Reacted (%) (without H_2)	(with H_2)
925	1	.5/0	14	16
925	2	.5/0	27	23
950	0.5	.5/0	21	17
950	1	.5/0	33	30
700	1	.5/3.5	21	23
700	2	.5/3.5	51	53
725	0.5	.5/3.5	27	30
725	1	.5/3.5	44	51
725	1	1/3.5	39	36

<u>Task 2</u>

This task consists of determining the rate and products of oxidation of HCN. Investigation of the rate of oxidation of HCN was initiated at 1073 K to determine if it was being consumed as it was being produced from pyridine and under what, if any, conditions NO can be produced from HCN at this low temperature. All the rate data will be tabulated in the next report, but some observations can be summarized at this point: (a) The rate of consumption of HCN was significant using oxygen at 3.5 or 7.0% concentrations. (b) Addition of benzene to produce an environment similar to that of pyridine oxidation tended to increase the rate of HCN oxidation up to an equivalence ration (ER) of about 0.9, after which the rates of consumption of both HCN and oxygen drastically fell off; no significant NO was noted at all ERs. (c) It was thought that possibly acetylene may have been an inhibiting intermediate, (the 26 ion current appeared large for high ER experiments) but a few experiments with added acetylene gave increased HCN consumption and also significant NO formation. It is clear from these observations that there is still considerable uncertainty as to the factors influencing NO formation.

Mechanism Discussion and Future Work

Although there is still much to be learned about this complex mechanism, some observations about the factors influencing NO formation can be made and attempt to relate these to staged combustion results. It is clear that inert pyrolysis of heterocyclic nitrogen leads to HCN as the only major volatile nitrogen containing product, with some nitrogen remaining in the solid, the fraction of which depends on the pyrolytic temperature. When the oxygen is added, the products are about the same for very fuel rich mixtures. However, as the concentration of oxygen is increased, the solids (smoke) production decreases while HCN yield appears to stay the same or increases a small amount. At ER $\geq$ 1 but with low oxygen concentrations, $\leq$ 7 mole %, the smoke becomes negligible but HCN yield still remains about the same, the rest of the product nitrogen appearing primarily as N_2. As the oxygen concentration increases with fuel lean mixtures, a shift in products occurs with nitrogen oxides becoming important. This is consistent with the data at 1223 K reported earlier (Table 1, ref. 2). It was found that fuel lean mixtures at 3.5% O_2 produced small amounts of NO (less than 15% of total nitrogen) and significant N_2, but at 7.0% O_2 all lean mixtures yielded significantly higher NO. Thus, at low temperatures higher concentrations of O_2 are necessary to activate the NO_x formation mechanism. In conclusion, it appears that if the proper oxidizing conditions are used, N_2 formation will be promoted at the expense of NO_x formation.

Future experiments will be concerned with the completion of the HCN oxidation kinetics study and a better definition of the conditions of concentration and temperature necessary to optimize N_2 production in the low temperature (973 to 1173 K) region.

REFERENCES

1. T. Houser, "Fundamentals of Nitric Oxide Formation in Fossil Fuel Combustion", FE-2018-14, June-Sept. 1979.

2. T. Houser and M. E. McCarville, Ibid, FE-2018-17, Mar.-June 1980.

3. T. Houser, Ibid, FE-2018-15, Sept.-Dec. 1979.

4. A. E. Axworthy and V. H. Dayan, Proceedings of the Second Stationary Source Combustion Symposium, Vol IV, p. 41, EPA-600/7-77-073d, July 1977.