Relative Significance of NO_x and HCN in Fire Gas Toxicity

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ABSTRACT

Analytical data on NO_x in the pyrolysis/combustion products of various materials have been available for some time. In this study, its generation is discussed, based on data obtained from the literature and the author's experiments. In these experiments, polyacrylonitrile fabric was burnt in: (a) a quartz tube, (b) an ASTM oxygen index test apparatus, (c) an ASTM (or Ohio State University) heat release rate apparatus, and (d) an ASTM full-scale room. The toxicity of NO_x was comparable to or less than that of HCN. Since concentrations of NO_x produced are normally much lower than those of HCN, NO_x would be expected to be of minor in fire gas toxicity considerations.

INTRODUCTION

Oxides of nitrogen (NO_x) include, NO, NO_2, N_2O_3, N_2O_4 or $(NO_2)_2$ and N_2O_5. NO and NO_2 are the most common among them, and therefore only these two will be discussed in this paper.

NO_x may be produced in two ways: by the oxidation of atmospheric N_2 at high temperatures (thermal NO_x), or by the pyrolysis and combustion of nitrogen-containing fuels (fuel NO_x). The generation of thermal NO_x in furnaces or internal combustion engines is of interest mainly in pollution control. In fire gases the thermal NO_x plays an unimportant part, because its formation in diffusion flames is insignificant (1). In this study the significance of fuel NO_x in fire gas toxicity will be discussed, based on analytical data obtained from the literature and in the author's laboratory. Special attention is paid to the relative importance of NO_x and HCN, both of which may be produced from the combustion of nitrogen-containing fuels.

Analytical data on NO_x generation

Some analytical data on NO_x produced in fire or in the pyrolysis/combustion of organic fuels, as reported in the literature, are listed in Table 1 (2-17). Most of them are presented either as quantities produced from a known weight of a fuel, or as gas phase concentrations. Direct comparison of these two kinds of data is difficult, since information necessary for converting from one to the other is often lacking. A high concentration of NO_x, 100 ppm or more, was found only in full-scale room experiments (No.

TABLE 1 GENERATION OF NOX IN FIRE EXPERIMENTS

NO. MATERIALS	ATMOSPHERE (A)	TEMP. (B)	NOX (C)	NOX/HCN (D)	GENERATION	NOX ANALYSIS	AUTHOR	YEAR	REF
1 CELLULAR ACRYLONITRILE			15.6		IN A GLASS BULB	HARGER & HULPIEU METHOD	WATSON	(1951)	2
2 CELLULAR PVC			8.8						
3 ABS			30PPM		NBS SMOKE CHAMBER	COLORIMETRIC TUBES	GROSS	(1968)	3
4 WOOL RUG			25PPM						
5 NYLON TYPE RESIN			50PPM						
6 COTTON			8PPM						
7 AROMATIC POLYAMIDE RUG			18PPM						
8 POLYETHER URETHANE FOAM			12PPM						
9 UREA-FORMALDEHYDE		500	5PPM	0.005	1G UNDER FLOW	COLORIMETRIC TUBES	BOTT	(1969)	4
10 UREA-FORMALDEHYDE	N2	500	2PPM						
11 POLYACRYLONITRILE	N2	500	20PPM						
12 POLYACRYLONITRILE		500	25PPM						
13 ACRYLIC FIBRE		600	15	(E)	8 TO 60MG IN A TUBE	COLORIMETRIC TUBES	SKIDMORE	(1974)	5
14 ACRYLIC FIBRE		800	11	0.04					
15 ACRYLIC FIBRE		1000	18						
16 NYLON		600	10						
17 NYLON		800	2.2	0.04					
18 NYLON		1000	8.8						
19 WOOL		600	2.4						
20 WOOL		800	1.6	0.02					
21 WOOL		1000	6.0						
22 POLYURETHAN FOAM		600	4.6						
23 POLYURETHAN FOAM		800	3.1	0.07					
24 POLYURETHAN FOAM		1000	4.7						
25 COMMERCIAL PRODUCTS			87PPM		FULL SCALE ROOM FIRE		ARMSTRONG	(1974)	6
26 TYPICAL ROOM			150PPM	0.2	FULL SCALE ROOM FIRE	ELECTROCHEMICAL & NDIR	HILLENBRAND	('74)	7
27 IMPROVED ROOM			100PPM	0.9					
28 SPACE-AGE ROOM			15PPM	6.5					
29 SYNTHETIC POLYMER F.R.			168PPM		10G WITH TORCH IN A BOX		MONTGOMERY	(1975)	8
30 NATURAL POLYMER			126PPM						
31 WOOL			10PPM		E-84 TUNNEL	COLORIMETRIC TUBES	PRYOR	(1975)	9
32 RED OAK			10PPM						
33 ACRYLIC CARPET			1PPM						
34 RIGID PU FOAM	PREHEAT 60		18PPM	0.6	NBS SMOKE CHAMBER	COLORIMETRIC TUBES	LEE	(1975)	10
35 RIGID PU FOAM	PREHEAT135		30PPM	1.7					

TABLE 1 CONTINUED

NO. MATERIALS	ATMOSPHERE	TEMP.	NOX	NOX/HCN	GENERATION	NOX ANALYSIS	AUTHOR	YEAR	REF
36 WOOL		800	5N%		MOVING SAMPLE BED	CHEMILUMINESCENCE	MUKAI	(1977)	11
37 DOUGLAS FIR			0.1PPM		3.5G UNDER FLAT HEATER	SALTZMAN COLORIMETRY	HARTUNG	(1977)	12
38 POLYURETHANE			2PPM						
39 FIR PLYWOOD	COMB.475		10PPM		2 TO 12G IN POTTS' POT	CHEMILUMINESCENCE &	POTTS	(1977)	13
40 RED OAK	COMB.480		10PPM			COLORIMETRIC TUBES			
41 POLYSTYRENE HIGH IMPACT	COMB.475		4.5PPM						
42 STYROFOAM	COMB.550		15PPM						
43 RIGID POLYURETHANE	COMB.560		95PPM						
44 RIGID POLYURETHANE	PYRO.560		<1PPM						
45 PVF/PHENOLIC PANEL		600	0.37	0.04	0.25G IN A TUBE	GRIESS-SALTZMAN METHOD	SPURGEON	(1977)	14
46 FR URETHANE FOAM		600	0.02	0.002					
47 AROMATIC POLYAMIDE		600	0.53	0.04					
48 FR WOOL		600	0						
49 PVF/PHENOLIC PANEL			0.01	0.02	NBS SMOKE CHAMBER				
50 AROMATIC POLYAMIDE			0.26	0.1					
51 FR WOOL			0.45	0.03					
52 COTTON BATTING	1.0W/CM2		10PPM(F)	2.7	OSU HRR IN 10 MINUTES	CHEMILUMINESCENCE	HERRINGTON	(1978)	15
53 ISOCYANURATE FOAM	1.0W/CM2		24PPM	1.5			(AND 1979)		
54 RIGID PU FOAM	1.0W/CM2		61PPM	1.8					
55 RESILIENT PU FOAM	1.0W/CM2		122PPM	4.9					
56 WOOL FABRIC			2.7(G)	0.09	BY A TRAVERSING FLAME	NO3 ELECTRODE &	HOSCHKE	(1981)	16
57 NOMEX FABRIC			6.0	1.1		CHEMILUMINESCENCE			
58 MODACRYL DRAPE			6.2	0.09					
59 FR PU FOAM			1.7	0.3					
60 WOOL FABRIC			9.3	26					
61 NOMEX FABRIC			28	2.2					
62 MODACRYL DRAPE			15	0.9					
63 FR PU FOAM			17	2.4					
64 HOUSEHOLD GOODS		870	90PPM	0.36	FULL SCALE ROOM FIRE	COLORIMETRY(H)	MORIKAWA	(1985)	17
		700	170PPM	3.7					

(A) ATMOSPHERE IS AIR UNLESS OTHERWISE SPECIFIED
(B) NOMINAL TEMPERATURE IN CENTIGRADE
(C) NO2/SPECIMEN IN MG/G UNLESS OTHERWISE SPECIFIED
(D) MOLE RATIO
(E) AVERAGE VALUES FOR THE MATERIAL
(F) ORIGINAL DATA WERE PRESENTED IN MG/MIN.M2
(G) ORIGINAL DATA WERE PRESENTED IN G/M2
(H) NAPHTHYL ETHYLENEDIAMINE

26, 27, 64 in the Table), in an Ohio State University heat release rate apparatus (No. 55), and in combustion experiments using a torch (No. 29, 30). The data on NO_x generation based on fuel weight may be compared with published data on HCN generation from similar materials under similar conditions (18). The quantities of NO_x generated are less than those of HCN, often by a factor of 10. The fuels listed in Table 1 are mostly nitrogen-containing polymers. Some non-nitrogen-containing polymers are also listed (No. 2, 6, 32, 37, 39, 40, 41, 42, 45, 49, 52); clearly, NO_x generation from the burning of such fuels is insignificant.

Mukai (11) burned wool at controlled air/fuel ratios. At 800 C, when the ratio was increased from 0 to 3, the conversion of fuel nitrogen to NH_3 decreased from 35% to 0%, while its conversion to NO increased from 0% to 5%. Mukai considered NH_3 as an intermediate compound in the conversion of fuel nitrogen to NO_x.

In studies of Axworthy et al (19), who pyrolyzed nitrogen-containing fossil fuels and model nitrogen compounds, HCN was considered to be the principal intermediate product in the formation of NO. In the absence of O_2, the yield of HCN, in terms of the mole ratio to fuel nitrogen, increased with temperature up to 50%. Under Axworthy et al's experimental conditions, i.e., at temperatures higher than 950 C, ammonia was produced in a minor amount. They speculated that in the presence of O_2, N_2 (and other nitrogen compounds) and NO were formed in competing reactions from the oxidation of HCN. In the studies of Herrington (15) (No. 52-55 in Table 1), who burnt several types of polyurethane foams in a horizontal position in an Ohio State University heat release rate apparatus at 1 W/cm" irradiation, relatively high concentrations of NO_x were found. NO_x was always produced in higher concentrations than HCN.

EXPERIMENTAL

Material

A commercially available Acrilan fabric (Type 16, Plain Weave, Test Fabric Inc., NJ, U.S.A.), containing more than 85% polyacrylonitrile (PAN), was used without further treatment. The density of the fabric was 0.20 kg/m".

Pyrolysis/Combustion

Four series of experiments were performed on the burning of the material according to the following schedule:

(a) Horizontal quartz tube. A 0.5 g specimen in a ceramic boat was heated in a 17 mm i.d. quartz tube in an electric oven, and burnt in an air current. The temperature of the oven was isothermally controlled at one of the following levels: 400, 600, 800 or 1000 C.

(b) Oxygen index (20). A 0.7 g specimen was burnt in vertical position in an O_2 + N_2 current at a supply rate of 300 mL/sec (or 4.7 cm/sec linear velocity). The O_2 percentage was 24, 21 or 18.

(c) Release rate (21). A 72 g specimen was burnt in vertical position under varied air flow rates (15, 30, 60, 120 L/min) and irradiations (1, 2.5, 4 W/cm").

(d) Full-scale room (22). In a standard size room (interior dimensions 3.7

x 2.4 x 2.4 m) with a single open doorway, two series of experiments were performed. In a vertical test series, 2 kg of Acrilan fabrics were stapled in two layers to the gypsum wallboard in a corner of the room. The fabric was ignited with a propane sand burner of heat output of 50 kW. In the second series, the same weight of material was burnt in horizontal position; it was placed in two layers on a steel grate (mesh size 2 cm x 4 cm) platform in the centre of the room. The ignition sources were methenamine tablets at five locations.

Analysis of HCN and NO_x

$\underline{NO_x}$. The combustion gas was collected in a 15 L polyethylene bag at a pumping rate of 2 L/min for 2.5 min, except in the experiments using the oxygen index tester, where all the exhaust gas from the apparatus was collected during the burning of the sample. In order to oxidize NO to NO_2 (23), sufficient amount of O_2 was added to the bag to raise its concentration to a level higher than 21%. After one hour, 25 mL of deionized water was added. Upon shaking the bag, NO_2 was absorbed in the water to form NO_2^- and NO_3^-. The ions were determined by ion chromatography (IC). The IC apparatus consisted of a Vydac Ion Exchange Column 302IC4.6, Rheodyne 7001 Auto Injector fitted with a 200 L loop, and a Vydac 6000CD conductivity detector. The mobile phase was 4 mmol phthalic acid solution buffered at pH 4.5 with sodium borate. The flow rate was 2 mL/min. The conductivity detector was calibrated with known amounts of $NaNO_2$ and $NaNO_3$. The results were spot checked with the colorimetric method of Jacobs and Hochheister (24).

$\underline{HCN}$. HCN in the combustion gas was trapped for a period of 30 seconds in a soda lime tube (3 mm i.d., 10 cm long, packed with 20-30 mesh soda lime) as the combustion gas was flowing at a rate of 0.5 L/min. The soda lime was emptied into 50 mL of deionized water. A few drops of 1% lead acetate solution were added to remove the sulfide ions present. Concentrations of CN^- were determined by a cyanide electrode method. A series of NaCN solutions of different concentrations were used in the calibration.

RESULTS

The experimental results are presented in Table 2 (a), (b), (c), (d) and Figure 1. In the horizontal tube experiments, which represented the burning condition commonly used by other researchers, the nitrogen in PAN molecules was converted mostly to HCN, especially at higher temperatures, as previously reported (18). The conversion of nitrogen to NO_x occurred to a much lesser degree. The mole ratio NO_x/HCN was 0.1 and 0.02 at 800 C and 1000 C, respectively. In the ASTM heat release rate apparatus experiments the conversion to NO_x was of the same magnitude, on an N-conversion basis, as that observed in the horizontal tube experiments, but the conversion to HCN was much lower. In the full-scale room experiments using propane burners, there was little generation of NO_x. When using methenamine pills, more NO_x and less HCN was formed. The rates of generation of gases are shown in Figure 1.

Toxicity values

According to the Threshold Limits Committee of the American Conference of Governmental Industrial Hygienists, "The chief toxic effect of NO has been ascribed to the formation of methemoglobin and subsequent action on the central nervous system. Animal experiment data indicate that NO is about

one-fifth as toxic as NO_2. The information available on the mechanism of NO intoxication suggests that in mixtures with CO, as well as NO_2, additive effects should be assumed" (25). Montgomery and others determined or estimated the one hour lethal concentration of several toxic gases: CO, 4000 ppm; HCN, 200-300 ppm; NO_x, 200-400 ppm (8). Higgins and others determined the 5 minute LC50 of several toxic gases for rats and mice respectively: NO_2, 831 and 1880 ppm; HCN, 503 and 323 ppm (26). Nishimaru et al determined the LC50 of six toxic gases using mice. The 30 minute LC50 values are: CO, 780 ppm; NO_2, 220 ppm; and HCN, 36 ppm (27). These data indicate that the toxicity of NO_x is comparable to or less than that of HCN.

Table 2(a)   Combustion of PAN in a Horizontal Tube

Temp. C	Air flow L/min	Sample g	N-conversion % NO_x	HCN	Total	NO_x/HCN
400	1	0.5	n.d.*	1.2	1.2	-
600	1	0.5	n.d.	2.4	2.4	-
800	1	0.5	0.3	3.3	3.6	0.1
1000	1	0.5	0.15	8.3	8.4	0.02

* not detected

Table 2(b)   Combustion of PAN in an ASTM Oxygen Index Test Apparatus

O2 %	Flow L/min	Wt.burned g	Burn time min	Conc. ppm NO_x	HCN	N-conversion % NO_x	HCN
18	18	0.386	3.17	4		0.16	
21	18	0.861	1.33	27		0.21	
24	18	0.766	1.10	24		0.17	
18	18	0.232	1.42		11		0.35
21	18	0.853	1.48		44		0.38
24	18	0.790	0.83		78		0.41

Table 2(c)   Combustion of PAN in an ASTM Release Rate Apparatus

Irradiation W/cm^2	Air flow L/min	Max. conc. ppm NO_x	HCN	N-conversion % NO_x	HCN	Total	NO_x/HCN
1	15	81	318	0.02	0.05	0.07	0.4
1	30	241	152	0.13	0.02	0.15	6
1	60	177	94	0.14	0.09	0.23	1.5
1	120	35	29	0.05	0.03	0.08	1.7
2.5	60	76	132	0.07	0.06	0.13	1.2
2.5	120	83	42	0.08	0.04	0.12	2.3
4	30	380	870	0.17	0.36	0.53	0.4
4	60	239	780	0.21	0.32	0.53	0.6

Table 2(d)   Combustion of PAN in an ASTM Full-scale Room

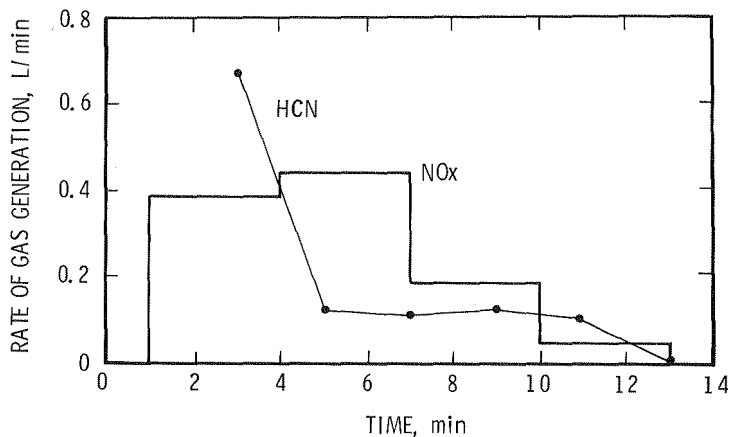| Ignit. source	Sample orient.	Sample kg	Max. conc. ppm* NO_x	HCN	N-conversion % NO_x	HCN	Total	NO_x/HCN
Pills	Horizontal	2	33	21	0.53	0.47	1.0	1.3
Pills	Horizontal	2	14	22	0.44	0.34	0.8	1.1
Propane burner	Vertical	2	2	56	0.02	0.68	0.7	0.03
Propane burner	Vertical	2	2	81	0.02	0.65	0.7	0.03

*Concentration in the exhaust duct

Figure 1 Rates of Generation of Gases in a Full-scale Room
PAN 2 kg was ignited with pills at horizontal orientation

DISCUSSION

For several materials listed in Table 1 (No. 36, 39-41, 52-55, 56-63), the
analytical data were obtained with a chemiluminescent analyzer. Such data
require careful examination. According to Felstead et al, HCN, aceto-
nitrile and other nitrogen compounds were converted to NO_2 (76 to 98% for
HCN and 102% for acetonitrile) in a chemiluminescent analyzer equipped
with a stainless steel high temperature vessel for the conversion of NO_2
to NO (28). HCN was often generated in pyrolysis and combustion in quanti-
ties larger than NO_x, as stated earlier in this paper. In the author's
studies, acetonitrile was generated in the combustion of PAN (26) and
other nitrogen-containing polymers, such as urea-formaldehyde resin,
nylons and polyurethane (unreported). Thus the chemiluminescence type NO_x
analyzer, when applied to fire gas analysis, may indicate much higher
total NO_x concentrations than are actually present.

Earlier studies (18) indicated that in the pyrolysis/combustion of
nitrogen-containing fuels the conversion of fuel nitrogen to HCN was
sometimes more than 50%. In the present study, the conversion to NO_x was
much less than 1%. Again, other data found in the literature suggest that
the mole ratio NO_x/HCN is often much smaller than unity. Ratios larger
than unity may be attributed to a low conversion to HCN. Such may be the
case when the flaming is not too brief, e.g. under 1 or 2.5 W/cm^2 irradi-
ation in the ASTM heat release rate apparatus. Herrington's experiments
with polyurethane foams (15) seemed to support this view. Similar results
were obtained in experiments conducted in the oxygen index test apparatus
and in the full-scale room fire experiments of the present study. At low
O_2 percentage in the former experiments and with horizontal position pill
ignition in the latter, the HCN concentrations were low. With moderate
flaming, there seems to be more chance for HCN oxidation to yield NO_x and
other compounds than with brisk flaming such as that occurring at 24% O_2
(Table 2(b)), under 4 W/cm^2 irradiation (Table 2(c)), or in the flame of a
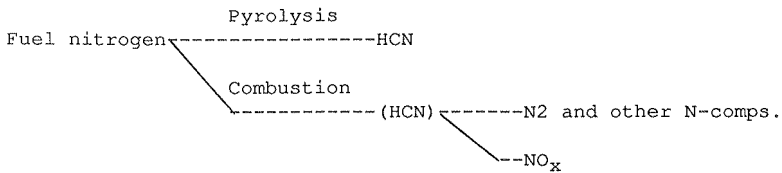hot propane burner (Table 2(d)).

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                    Pyrolysis
Fuel nitrogen╲----------------HCN

              ╲  Combustion
               ╲----------(HCN)╲------N2 and other N-comps.

                                  ╲--NOₓ
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Figure 2   Hypothesis for NO_x and HCN Generation

Based on the experimental data and the hypothesis of Axworthy et al (19), the HCN and NO_x generation may occur as shown in Figure 2. A lower percentage of fuel nitrogen will appear as NO_x from combustion than as HCN from pyrolysis. Since the toxicity of NO_x is comparable to or less than the toxicity of HCN, NO_x is less important than HCN from the point of view of fire gas toxicity.

CONCLUSIONS

According to the literature, less NO_x than HCN (on an N-conversion basis) is generated in the pyrolysis/combustion of nitrogen-containing fuels. In some studies that reported high yields of NO_x, still less NO_x relative to HCN might in fact have been generated since some chemiluminescence type NO_x analyzers may give exaggerated NO_x values in the presence of HCN and acetonitrile. In the author's experiments, conversion of fuel nitrogen to NO_x was, except in one case, much less than 1%. In contrast, conversions to HCN as high as 50% have been reported in the literature. In a moderate flaming combustion, the NO_x/HCN ratio may become larger than unity, because there is more time for HCN oxidation. Since the toxicity of NO_x is comparable to or less than that of HCN, and since less NO_x than HCN is produced, the part played by NO_x in fire gas toxicity is of secondary importance to that of HCN.

ACKNOWLEDGEMENT

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