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Studies of Toxic Gas Production During Actual Structural Fires in the Dallas Area

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ABSTRACT: Gases produced during structural fires were studied as to their potential toxicities. Carbon monoxide was the only gas measured in concentrations considered to be lethal within a short period of time. No correlations were found between gases produced and materials burning. However, significant correlations were discovered between gases produced and the physical aspects of the fire (intensity, burning rate, and the like). The organic compounds identified within the gases gave insight as to another potential health hazard not yet considered. These organic compounds are the products of free radical reactions and as free radicals their potential as toxics is enormous.

KEYWORDS: forensic science, fires, gases

The materials surrounding us contain a great variety of combustible solids. Many are used as blends or composites or contain fillers or additives of many types. One cannot explain the behavior of combustion products in terms of relatively pure substances, such as cotton, polystyrene, and the like. In reality, one is concerned with a gross mixture of many substances.

The simplest imaginable solid ignites and burns with far greater complexity than a gaseous fuel. Since the solids we are concerned with must volatilize to form gases before combustion can occur, all the complexities of gaseous combustion are present; in addition, certain characteristics of the solid must be considered. These characteristics include transient thermal response, pyrolysis thermodynamics, pyrolysis kinetics, radiation properties at surface diathermanous properties, thermal conductivity, melting, and char formation. About 1932, the first qualitative insight into the hydrogen-oxygen combustion via a branched chain reaction involving atomic hydrogen, hydroxyl, and atomic oxygen species was just emerging. A quantitative understanding was reached only in the mid-1960s. The methane-oxygen reaction is more complex and was not completely understood until the 1970s [1]. Figure 1 conveys some ideas of their complexities.

Limited studies have been conducted for the identification and measurement of air con-

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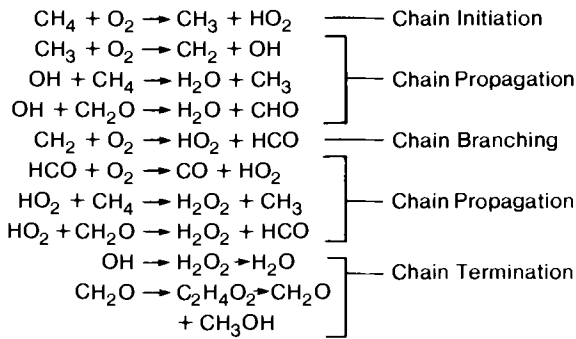


FIG. 1—Major reactions involved in the oxidation of methane.

taminants in actual fire scenes. A study was reported in 1973 of the exposure of working firefighters to carbon monoxide and oxygen [2,3]. For this study, a series of 72 residential fires were monitored by using a portable recording sampler worn by firefighters. The maximum carbon monoxide concentration noted during the study was 27 000 ppm. In only six fires did the oxygen concentration fall below 18%.

In a similar study [4], carbon monoxide was again identified as the most important air contaminant; oxygen levels remained between 19 and 21%. Carbon dioxide concentrations were reported as less than 1.5% in all cases. The carbon monoxide readings ranged from 0 to more than 15 000 ppm. Total hydrocarbons were measured in the range of 300 to 700 ppm. Nitrogen oxides and halides were not detected in this study and were reported as being below the sensitivity of the equipment used for the analysis (10 ppm and 5 ppm, respectively). Investigators at The John Hopkins University reported a series of studies emphasizing biological monitoring of firefighters and fire victims for carbon monoxide, hydrogen cyanide, heavy metals, and particulates [5,6]. More recently, investigators at Harvard University completed a study of the concentrations of carbon monoxide, carbon dioxide, oxygen, hydrogen chloride, hydrogen cyanide, and nitrogen dioxide encountered during fire fighting [7,8]. This study shows carbon monoxide to be the only significant acutely toxic gas produced in fires. These data suggest the possibility that acrolein might be an acute problem in a very small percentage of cases. However, many aldehydes are quite common in fires, as would be expected (see Fig. 2). A study of real fire atmospheres in single-family, one-story frame houses in San Antonio, TX was conducted [9,10]. The majority of samples reported in this study indicated the atmospheres not to be acutely toxic. A small percentage of the samples indicated sufficiently high concentrations of toxic substances to cause acute toxic effects. Again, carbon monoxide was the major toxic component produced by the fire.

In no instance in the above-noted studies was hydrogen cyanide found in sufficient quantity to be considered a hazard in a real fire situation.

The present study was undertaken in actual structural fires to:

1. determine what gases were produced;
2. quantitate these gases in smoke;
3. determine, if possible, which gases may be capable of producing acute toxic effects, based on the known effects of these substances; and
4. predict, if possible, whether any of the toxic substances was present in sufficient concentration to affect the escape of persons from this fire (smoke) environment.

To do this, it was necessary to view fires in terms of an energy spectrum, ranging from areas of intense heat to areas having cooler temperatures. The areas where samples were to be taken were defined as areas with light to dense smoke concentrations, but with relatively low

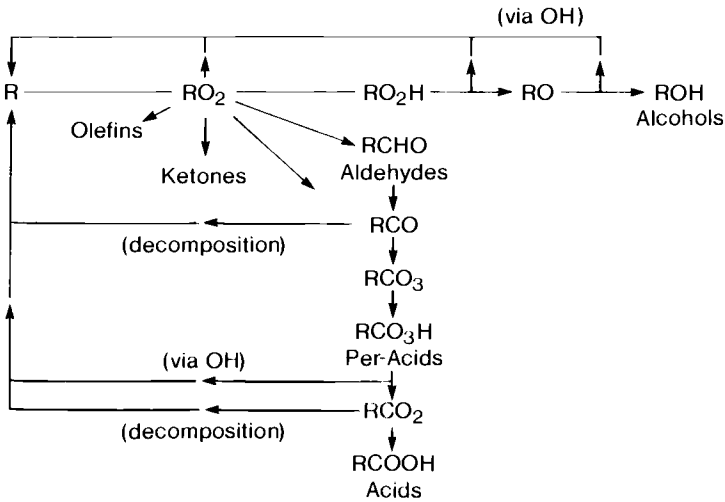


FIG. 2—Summary of principal chemical reactions involved in hydrocarbon reaction.

thermal energy (for example, situations, where the heat of the environment was relatively low, making it impossible for a person to be injured by the fire itself).

Experimental Procedures

All gases used for calibration purposes were obtained from Air Products and Chemicals, Inc.

Gas samples were analyzed in the laboratory with a Miran IA general purpose gas analyzer produced by Foxboro Analytical Co. This infrared gas analyzer is a single-beam, variable filter spectrometer, scanning the infrared spectral range between 2.5 and 14.5 μm. The instrument is equipped with a gas cell having a path length variable between 0.75 and 20.25 m. The infrared gas analyzer was equipped with a strip chart recorder for recording all absorbance values. The following parameters were used for the gases analyzed:

- Carbon monoxide: wavelength, 4.61 μm; path length, 20.25 m; absorbance, 0.045; minimum detection, 0.2 ppm.
- Hydrogen cyanide: wavelength, 3.94 μm; pathlength, 20.25 m; absorbance, 0.0083; minimum detection, 0.4 ppm.
- Formaldehyde: wavelength, 3.58 μm; pathlength, 20.25 m; absorbance, 0.015; minimum detection, 0.2 ppm.
- Acetaldehyde: wavelength, 9.0 μm; path length, 20.25 m; absorbance, 0.23; minimum detection, 0.08 ppm.

The firefighters wore Model TD Monitaire samplers, with the gas sampling pump calibrated and adjusted to pump 0.7 L of air per minute. These pumps were obtained from the Mine Safety Appliances Co. (MSA). One pump was utilized for multiple colorimetric detector tubes, using the multiple tube assembly with the carbon monoxide tube (No. 91229 MSA), the hydrogen chloride tube (No. 91636 MSA), the hydrogen cyanide tube (No. 93262 MSA), and the formaldehyde tube (No. 93963 MSA). The second pump was rigged with the MSA charcoal sampling tube holder with MSA charcoal sampling tubes.

In addition, the firefighters used the following equipment for gas grab sampling in the fires:

1. a 500-mL gas collecting tube with a Teflon® stop cock (Kimble 30040-F);
2. a 140-mL disposable syringe; and
3. 3.8-L (1-gal) paint-type can with triple friction top.

These gas samples were analyzed for carbon monoxide, hydrogen cyanide, formaldehyde, and acetaldehyde by gas infrared spectrometry. The values were compared with the colorimetric tubes values obtained by the firefighters. The organics were analyzed in each grab sample by gas chromatography/mass spectrometry (GS/MS) as described below. The results were compared to each on-site survey and to the carbon disulfide extraction of the charcoal tubes collected by the firefighters.

The organic analyses were conducted by computer-interfaced GC/MS utilizing a Finnigan MAT 1000 series OWA automatic GC/MS system. The gas chromatography was performed with a 1.8-m (6-ft) glass column with a 2-mm inside diameter, packed with 0.2% Carbowax 1500 on Carbowax C (60/80 mesh). The temperature was held at the 60°C for 3 min, then raised 8°C/min to the final temperature of 160°C with a final time of 15 min. The carrier gas was high-purity grade helium, flowing at 20 mL/min.

The mass spectrometry conditions were as follows: electron energy, 70 V; mass range, 35 to 260 AMU; scan time, 2 s; number of scans acquired, 900; threshold, 1; minimum peak area, 10; separator oven, 250°C; manifold temperature, 80°C; and solvent divert valve time, 0 s.

The gas chromatograph/mass spectrometer was equipped with a Tekmar Model LSC-2 liquid sample concentrator with a 25-mL sampler and Tenax-Silica gel trap column. The purge rate was 40 mL/min with a purge time of 10 min at 30°C. The desorb time was 4 min at 180°C and the bake time was 3 min at 225°C.

All gas samples for analysis were handled with a 30-mL Hamilton Gas tight syringe with a Teflon Luer Lock and a 20-gage lumbar needle.

To analyze the samples, a 25-mL sample of air was added to specially designed glass purging chamber at ambient temperature. An inert gas, helium, moved the volatiles in the air sample through a sorbent column, where the volatiles were trapped. After purging was completed, the sorbent column was heated and back-flushed with the inert gas to desorb the volatiles onto a gas chromatographic column. The gas chromatograph was temperature programmed to separate the volatiles, which were then detected with the mass spectrometer.

Results

Table 1 outlines the results of this study. The guidelines used to evaluate the potential health impact of each gas studied were the same as in previous studies [8, 9].

Three guidelines were used to evaluate the potential health impact of the air contaminants encountered in fires. The first were those of the American Conference of Governmental In-

TABLE 1—Summary of observations.

Gas	Maximum, ppm	Range, ppm	Average, ppm	STEL, % ^a	IDLH, % ^a	STLC, % ^a
Carbon monoxide (CO)	15 000	0-15 000	1450	28.5	10.5	10.5
Hydrochloric acid (HCl)	40	0-40	1.1	2.6	0	0
Hydrocyanic acid	40	0-40	3.7	10.5	0	0
Aldehydes (formaldehyde and acetaldehyde)	15	1-15	5	2.5
Total hydrocarbons	1200	500-1200	800

^aLevel observed in percent of samples analyzed.

dustrial Hygienists, which publishes a list of threshold limit values—short-term exposure limits (TLV-STEL, or simply STEL) [11]. These limits refer to airborne concentrations of specific contaminants and assume exposure to only a single substance. The definition of a STEL is:

The maximal concentration to which workers can be exposed for a period of up to 15 minutes continuously without suffering from (1) irritation, (2) chronic or irreversible tissue change, or (3) narcosis of sufficient degree to increase accident proneness, impair self-rescue, or materially reduce work efficiency, provided that no more than four excursions per day are permitted, with at least 60 minutes between exposure periods, and provided that the daily TLV-TWA [Time Weighted Average] also is not exceeded. The STEL should be considered a maximal allowable concentration, or absolute ceiling, not to be exceeded at any time during the 15 minute excursion.

The STELs were developed for unprotected industrial workers. Although it is unwise to use these numbers as an absolute value in a fire environment, considering the high concentration of gaseous compounds present, the STELs provide an excellent focal point for toxicological interpretations.

The second group of useful industrial exposure guides utilized were the concentrations at which the substances pose an immediate danger to life or health (IDLH) [8]. This index has been used in the Standards Completion Project of the National Institute on Occupational Safety and Health in defining the application of respiratory protection devices. The IDLH is defined as the concentration from which a worker might escape within 30 min without irreversible health effects or any physiological effects that would impede escape.

The major puzzling question for investigation of fire deaths is what events are occurring and what toxic substances are present over a short period. The values used by Terrill [12] in defining the short-term (10 min) lethal concentration (STLC) represent an excellent standard for fire health evaluation.

Carbon Monoxide

In all of the fire environments studied in the Dallas area, carbon monoxide (CO) levels exceeded the STEL (400 ppm) in an average of 28.5% of the fires studied. Only 10.5% of the fires produced CO levels exceeding the IDLH (1500 ppm) and the STLC (5000 ppm).

Hydrogen Cyanide

Hydrogen cyanide was detected in only 12% of the fires studied. The maximum concentration noted was 40 ppm. Only the STEL (15 ppm) was found, in 10.5% of the fires. The IDLH (50 ppm) and the STLC (350 ppm) were not found in any of the fires studied.

Hydrogen Chloride

In all the fire studies, hydrogen chloride (HCl) was detected in only 9%, with a maximum concentration of 40 ppm encountered on one occasion. The average HCl concentration found was 1.1 ppm, with only 2.6% of the fires exceeding the STEL (5 ppm). There were no fires studied where the IDLH (100 ppm) or the STLC (500 ppm) concentrations were detected.

Aldehydes

Our study was limited to formaldehyde and acetaldehyde, whereas other studies focused in on the aldehyde acrolein [8-10]. Although the aldehydes in our study were found in every fire sample, only 2.5% of the fires had concentrations greater than the STEL (10-ppm) concentrations.

Organic Compounds

The first phase of this study, which covered a limited number of fires, produced no significant pattern of decomposition of the organics.

As shown in Table 2, studies during Phase 1 indicated no pattern in the types of material burning. For example, the case number listed as DFD 17743 was a two-story old frame apartment building containing very few modern synthetic materials. The primary fire involvement was wood furnishings. Most contents were old, with very few new synthetic materials involved. In contrast to this were DFD 14767, a fire involving a chemical company that made paint additive, and DFD 14203, which involved one floor of a new high-rise office complex containing numerous modern synthetic furnishings. The first two fires were of the same relative intensity, whereas the latter was a less intense fire. Case 19000 was sampled 30 min after the fire was extinguished.

The second phase study, covering 75 fires, was used to compare sampling methods, gas concentrations, and decomposition patterns of the organics. Table 3 summarizes the 75 studies during Phase 2. These fires produced no significant patterns of organics as to the types of material burning. Like Phase 1, however, the comparison of the intensity of the fires, as judged by the Dallas Fire Department research group, showed significant patterns of similarities in organic products produced.

Discussion

The United States annually records more than 12 000 lives lost to fire. Some are attributed to the heat, either as direct burns or thermal shock. Other deaths result from carbon monoxide poisoning, as substantiated by a high carboxyhemoglobin (COHb). However, a large number of cases, such as the MGM Grand Hote fire, which involved 85 fatalities, have carboxyhemoglobin levels in a range that most forensic pathologist and toxicologists would call sublethal concentrations.

As noted above, many studies have been conducted regarding the toxic gases produced in fires. However, to date no data have been produced that show that in actual fire situations gases other than carbon monoxide are produced in concentrations high enough to be termed toxic to human beings.

To understand more fully the variables in fires of different types, we undertook to study the organic intermediates as well as many of the suspected toxic gases produced in fires. As is well known, a vast majority of gas-phase reactions produced by thermal initiation involve free-radical species as reactive intermediates. The presence of free radicals in such systems has long been recognized, but their importance and the decomposition of various types of materials have not been investigated. Therefore, in certain types of fires or certain types of materials whose burning produced unique organics, one could estimate the reaction products from thermal pyrolysis of these materials by investigating the thermochemistry and kinetics of the materials involved in the fire situation.

Carbon Monoxide

Carbon monoxide is an odorless and colorless gas with a specific gravity of 0.97. Kinetically, it is the bottleneck of combustion. Therefore, based on combustion kinetics, it is not unusual to find carbon monoxide as the major gas produced in fires, with the exception of high-energy reactive intermediates.

Carbon monoxide is toxic because of its special affinity for hemoglobin. It binds to hemoglobin with an affinity 250 times greater than that of oxygen. The result of that binding is carboxyhemoglobin (COHb). Hemoglobin becomes 50% saturated with oxygen at a partial pressure of 4 kPa (30 mm Hg), and with carbon monoxide at a partial pressure of 13.3 Pa (0.1 mm Hg). In addition, CO binds to myoglobin in muscle and to intracellular cytochrome

TABLE 3—Results of Phase 2.

Substance	Dallas Fire Department Incident No.							
	38334	38986	39214	39638	39742	39918	39986	40473
1-Propene	•		•	•		•	•	•
Chloromethane				•		•	•	•
Propane						•	•	•
Dichlorodifluoromethane		•				•		
Ethanol							•	•
2-Butene	•		•	•	•	•	•	•
1-Butene	•						•	•
Dichloromethane			•	•			•	
1,3-Butadiene	•			•			•	
2-Propanone	•	•	•	•		•	•	•
Furan	•						•	
Trichlorofluoromethane					•			
1-Isocyano butane				•				
Butane				•	•			
Acetic acid, methylester	•							
Cyclopentane				•				
3-Penten-1-yne or 1,3-cyclopentadiene	•			•			•	
1,2-Dimethyl cyclopropane			•	•		•	•	
2-Methyl butane	•	•	•	•	•	•	•	•
2-Methyl-1-butene	•	•	•				•	
Trichloromethane		•	•	•			•	•
Pentane	•	•	•	•	•	•	•	•
1,3-Pentadiene	•						•	
Cyclohexane	•	•		•	•	•	•	•
Ethyl cyclopentane				•	•	•	•	•
2,3-Dimethyl pentane	•	•		•	•	•	•	•
2,5-Dimethyl furan	•							
3-Ethyl pentane	•	•		•	•	•	•	•
3-Methyl hexane	•	•	•	•	•	•	•	•
2-Methyl hexane	•	•	•	•	•	•	•	•
Heptane	•	•		•	•	•	•	•
Toluene	•		•	•	•		•	•
2,2-Dimethyl hexane	•	•		•	•	•	•	•
2,4-Dimethyl hexane	•	•		•	•	•	•	•
2,3-Dimethyl hexane	•							
2,5-Dimethyl hexane	•	•		•	•	•	•	•
2,2,4-Trimethyl pentane		•	•					
Trimethyl-bicyclo heptane	•						•	•
2-Methyl-2-hepten-4-one	•						•	
Ethyl benzene	•		•	•			•	•
2,3,5-Trimethyl hexane	•				•	•	•	•
Dimethyl-methylane-bicyclo heptane							•	•
2,4-Dimethyl heptane	•			•	•	•	•	•
1,3-Dimethyl benzene	•						•	•
1-Heptane				•				
Cyclohexadiene	•					•	•	
2-Propanol								•
1-Butanol								•
2-Butanone								•
2-Methyl furan	•	•		•	•	•	•	•
2-Methyl-2-propanol							•	
1,2-Pentadiene or 1,4-pentadiene	•						•	
2-Pentene		•		•				•
2-Methoxy-2-methyl propane		•	•					

TABLE 3—Continued.

Substance	Dallas Fire Department Incident No.							
	38334	38986	39214	39638	39742	39918	39986	40473
1,4-cyclohexadiene	•							
Butonic acid	•							
Methyl cyclopentane			•	•				
2,3-Dimethyl-1-butene or 2-methyl-2-pentene				•				
2-Methyl pentane or tetrahydro-2-methyl furan		•	•	•		•		
3-Methyl pentane		•	•	•				
Benzene	•		•	•	•	•	•	•
1-Hexene	•		•	•			•	•
1-Isocyanato-2-methyl propane				•				
3-Methyl-3-buten-2-one or 3-penten-2-one	•							
1,1-Dimethyl cyclopentane		•		•		•		
1,3-Dimethyl cyclopentane	•	•		•		•	•	•
Hexane			•					
2-Hexene			•	•				
1,2-Dimethyl cyclopentane	•	•	•	•		•	•	•
Methyl cyclohexane	•	•		•		•	•	•

oxidases (especially cytochromes a₃ and P-450), thereby blocking cellular oxidation and causing cellular anoxia. Another cause of toxicity is the action of carbon monoxide on the disassociation of oxyhemoglobin: by reducing oxygen tension, it lowers the partial pressure at which oxygen is available to the tissues and results in a profound hypoxia early in carbon monoxide poisoning. Children appear to be particularly susceptible to CO poisoning, because of their lower hemoglobin concentrations and increased basal metabolic rate [13].

The level of carboxyhemoglobin achieved in the blood is a function of both the inspired concentration of CO and the duration of exposure. Figure 3 describes the speed and saturation of hemoglobin with different concentrations of CO, while Fig. 4 shows the percent of carboxyhemoglobin and symptomatology as a function of CO concentration and duration of exposure [14].

At a level of carboxyhemoglobin less than 10%, a person may manifest psychomotor and judgment inefficiencies. At a level of 10 to 20% exertional dyspnea is present; at 20 to 30%, headaches; at 30 to 40%, nausea, dizziness, and muscular weakness; at 40 to 50%, syncope; at 50 to 60%, convulsions; at 60 to 70%, coma and with long exposure death; and at 80%, instant death [15]. However, in several more recent fire death cases, blood carboxyhemoglobin levels have indicated percentages much lower than expected. Examples include the MGM Grand fire in Las Vegas, NV; the Hilton fire in Houston, TX; and the Ramada Inn fire in Forth Worth, TX.

The classic cutaneous sign—a cherry red color of the mucous membranes and lips—is variable. A child with severe carbon monoxide poisoning is more likely to be seen with a picture of toxic-metabolic encephalopathy often with associated injury to heart, lungs, extremities, and kidneys. The central nervous system and myocardium are most sensitive to the oxygen deprivation of carbon monoxide poisoning.

Obviously, with many deaths from smoke inhalation resulting in these lower carboxyhemoglobin levels, there must be an unknown second factor that has not been described. The explanation that is introduced in this paper suggests concern for chronic as well as acute exposures.

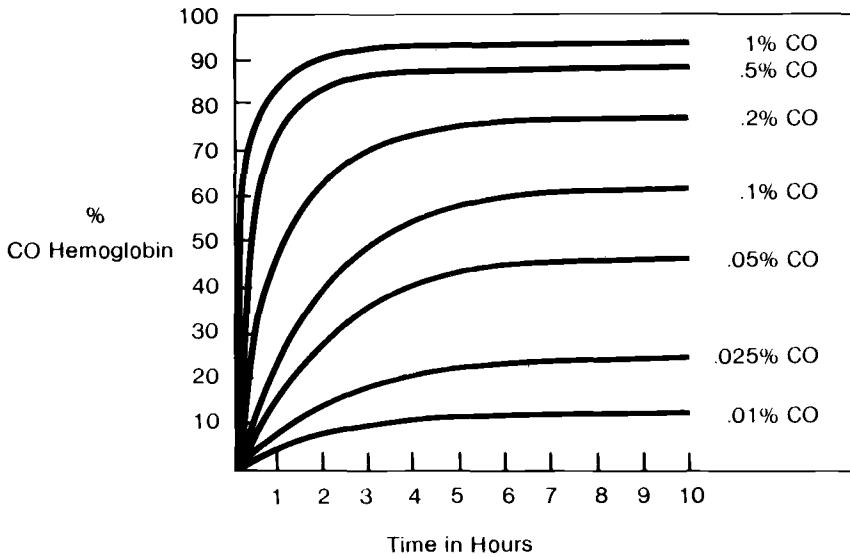


FIG. 3—Speed of saturation of hemoglobin with different concentrations of CO [14].

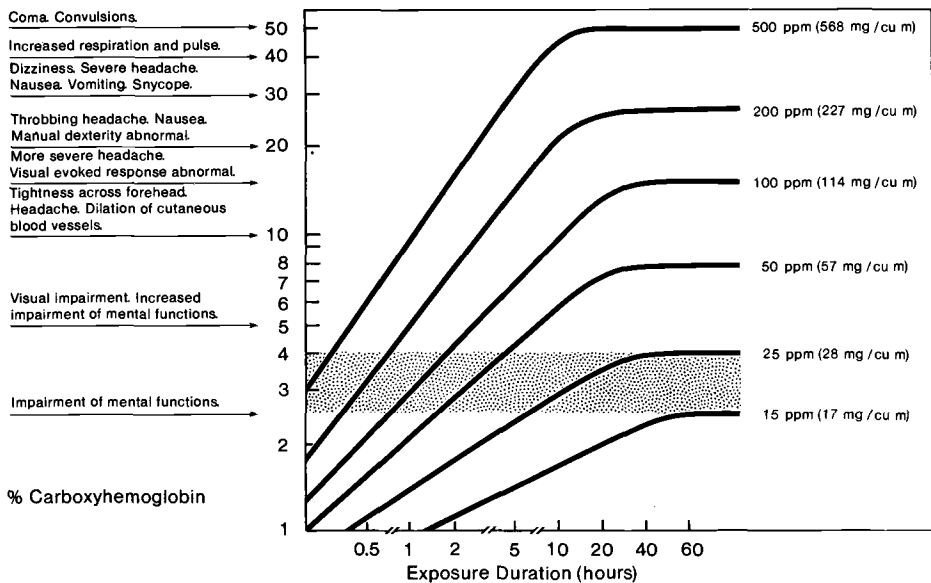


FIG. 4—Percent COHb and symptomatology as a function of CO concentration and duration of exposure [13].

Hydrogen Cyanide

The inhalation of cyanide gas represents of potentially rapid fatal type of exposure. Toxic symptoms may be observed at blood cyanide levels greater than 0.2 mg/L. Clinically, these symptoms are presented as salivation, nausea without vomiting, anxiety, confusion, vertigo, giddiness, lower jaw stiffness, convulsions, paralysis, coma, cardiac arrhythmias, and transient respiratory stimulation followed by respiratory failure.

Cyanide interrupts electron transport down the cytochrome chain by inhibiting at the cytochrome a-cytochrome a₃ step. Since the cytochromes are associated within a single unit, they are termed cytochrome oxidase. Oxidative metabolism and phosphorylation are compromised and electron transfer to molecular oxygen is blocked. The peripheral tissue oxygen tensions begin to rise and the unloading gradient for oxyhemoglobin is decreased [16].

In similar studies, hydrogen cyanide was detected in low concentrations in approximately 10 to 50% of the fires studied, but never in concentrations considered to be lethal [8-10, 17].

Two commercial aircraft accidents in the United States during the 1960s (Denver, CO, 1961; Salt Lake City, UT, 1965) contributed greatly to the initiation of the present concern over the toxic hazard of the gases generated in fires, and cyanide specifically. These accidents were of special significance because careful analysis indicated that few, if any, of the occupants could have suffered significant physical injury from the relatively mild impacts involved, yet a total of 60 persons perished as the result of thermal and chemical injuries sustained in the ensuing fires.

Hydrogen Chloride

Airborne hydrogen chloride exists in the anhydrous state and as a hydrochloric acid aerosol, that is, as microdroplets of a solution of hydrogen chloride and water. Because anhydrous hydrogen chloride is highly hygroscopic, exposure to this material is potentially more dangerous to the biologic system than exposure to hydrochloric acid aerosols. It injures not only by corrosion, as does the acid, but also by desiccation. This very affinity for water, however, makes general environmental chronic exposure to low concentrations of anhydrous hydrogen chloride extremely unlikely.

In other studies, HCl was present in over one third of the fires studied. In the majority of these fires, the concentrations were within the STEL range. Such concentrations would be sufficient to impede the escape of a person not wearing respiratory protection, but would not be considered lethal over a short period of time [8-10].

Aldehydes

Numerous aldehydes are produced in the process of combustion (see Fig. 2). Aldehydes produce four basic types of physiological effects. The first effect is the primary irritation of the skin, eyes, and mucosa of the respiratory tract. The second effect is the sensitization effect, primarily observed with liquid solutions. The third effect is the anesthesia effect and the fourth is the organic pathology. The latter has been experimentally produced in animals exposed to aldehyde vapors and involves damage to the respiratory tract and pulmonary edema [8].

Acrolein is a more toxic aldehyde than formaldehyde and acetaldehyde. Because of this, the Harvard study focused on acrolein. It was detected above the STEL (0.3 ppm) in 56% of the fires and above the IDLH (5 ppm) in 4.2% of the fires. In one fire, the concentration of acrolein was at the upper end of the STLC range (30 to 100 ppm) [8]. This was the first time that acrolein had been identified in life-threatening concentrations in real fires.

Organic Compounds

The organic compounds identified and shown in Tables 2 and 3 are the result of pyrolysis of the materials within the buildings. Although high concentrations of these organic compounds would produce drowsiness, nausea, headache, and finally unconsciousness and death from respiratory paralysis, the concentrations we observed were much lower.

The significance of the organics, however, is the mechanism by which these products are produced. Thermal pyrolysis and degradation proceed through free radical intermediates.

Organic Free Radicals

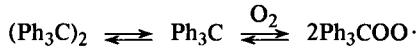
Several mechanisms have been proposed for the thermal initiation process, the most likely of which are the bimolecular reaction



and the termolecular reaction



Organic compounds with a weak C—C bond—for example, hexaphenylethane—may dissociate thermally to provide a significant source of free radicals:



The termolecular initiation reaction is basically thermochemically more feasible. Kinetics favoring this reaction have been demonstrated for the autooxidation of tetralin, cyclohexanol, and cyclohexanone.

As mentioned earlier, there are several physical characteristics that must be considered for the burning of solid materials. To understand why organic compounds escape the burning process, one must understand some of the physical factors taking place within the fire. Such factors include the pyrolysis gas concentration in the boundary layer, heat transfer from flame to surface, internal heat transfer, radiant loss from surface, and radiant flux from surroundings to surface. Therefore, the escaping velocity of the organic compounds in the vapor phase will be controlled by the piloted ignition temperature. Table 4 shows a few examples of organic compounds that were identified in abundance in this study and their thermal ignition temperatures. The limiting oxygen index tests shows that many thermoplastics in a candle form can be ignited and will sustain combustion in atmospheres containing appreciably less than 21% oxygen, while sustained candle-like burning of a small wood stick requires as much as 28% oxygen [1]. This difference may be primarily due to radiative loss from the burning surface; the plastic surface is at roughly 400°C, while the charred wood is at perhaps 600°C. Figure 5 sets forth the chemical kinetics of hydrocarbon oxidation. If one utilizes this concept and the heats of formation of various organic compounds with their autoignition temperatures, the rate of production of organic compounds or organic free radicals may be estimated. By studying these rates and the relative stabilities of organic free

TABLE 4—Comparison of temperatures required to oxidize various compounds to CO_2 and H_2O [18].

Compound	Ignition Temperature, °F ^a	
	Thermal	Catalytic
Benzene	1076	575
Toluene	1026	575
Xylene	925	575
Ethanol	738	575
MIBK	858	660
MED	960	660
Methane	1170	932
Carbon monoxide	1128	500
Hydrogen	1065	250
Propane	898	500

^a $t^\circ\text{C} = (t^\circ\text{F} - 32)/1.8$.

OVERALL REACTION	
COMPLETE COMBUSTION	$C_aH_b + (a + \frac{b}{4}) O_2 = aCO_2 + \frac{b}{2} H_2O$
INCOMPLETE COMBUSTION	$C_aH_b + \frac{a}{2} O_2 \rightarrow aCO + \frac{b}{2} H_2$
$\alpha F + \beta O_2 \rightarrow$ Products	F = Hydrocarbon Fuel α, β = Stoichiometric Factors
RATE OF DISAPPEARANCE	$\frac{1}{\alpha} \frac{dn_1}{dt} = -kn_1^\alpha No_2^\beta$
ARRHENIUS FORM	$K = A e^{E_A/RT}$ $K = BT^m e^{-E_B/RT}$ $A = BT^m e^m$ $E_A = E_B + mRT$

FIG. 5—Chemical kinetics of hydrocarbon oxidation [18].

radicals versus the toxicity of the atmosphere produced, one should better understand the concept of combustion toxicology.

In all the fires studied in the Dallas area, the concentrations of carbon monoxide, hydrogen cyanide, hydrogen chloride, aldehydes, and organic compounds varied relative to the physical aspects of the fire. There was no correlation with the burning of synthetics versus burning of wood products in the production of any of the above gases. The production of organic compounds followed the thermochemistry of organic pyrolysis. Many of the organic compounds identified would be the product of free radical rearrangements. This would explain why wood products would produce benzene, just as would synthetic products.

The reaction of organic free radicals with molecular oxygen, extra or intracellular, would theoretically be a logical explanation to the potentiation of the anoxic effects produced by carbon monoxide. These issues will be addressed in later studies.

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