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VOLATILE COMBUSTION PRODUCTS OF POLYVINYL CHLORIDE

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Abstract - The decomposition products that are evolved when heating or burning polyvinyl chloride or its plastics, both in air and in the absence of air, have been analyzed by several investigators. In recent years, much of this work has been directed to those compounds known to be toxic to man. As many as seventy-five compounds have been detected, more than fifty of which have been identified. Quantitative analyses have been carried out on many of these under various burning conditions. The effects of varying the temperature, the rate of burning, and the amount of air available are summarized.

INTRODUCTION

The polymer chemist has been interested in the pyrolysis products of polymers for a number of years, using the data generated to elicit information concerning polymer structure, as well as to determine the effects of various additives. More recently, the environmentalist has displayed an interest in the products of combustion, from the standpoint of the environmental and health hazards of such products. In our present environment, plastics are combusted intentionally (for disposal) or accidentally, such as in fires involving homes, industry, and transportation, with the evolution of toxic products.

One of the first polymers that received the attention of environmentalists was polyvinyl chloride (PVC). This interest stemmed from the prior knowledge that hydrogen chloride was a principal product of combustion, and from the fact that a considerable amount of this polymer goes into applications where an exposure to high temperatures is a possibility. Examples of this are plastic formulations for floor tiles and wire insulation, both of which can be involved in accidental fires. Besides the hydrogen chloride, it was soon learned that amounts of carbon monoxide and benzene, both toxic compounds, are also generated in such combustion processes. Also speculation of phosgene generation continues to arise. Esch and Dyer (1) report on a study of firemen exposed to the combustion products of PVC in the course of fighting fires, and describe the symptoms and signs of an "intoxication syndrome" associated with this type of exposure. A review of other studies of this problem of human exposures to PVC fire products is incorporated in a report by Tewarson (2).

In 1963, we began a program to determine the volatile combustion products of various plastics, concentrating our effort on those evolved compounds that are known or suspected to be toxic. Our first investigations were directed to polymers and plastics of polyvinyl chloride, resulting in a publication that appeared in 1969 (3). Since that time, further work has been carried out on the same polymer, the most recent on meat-wrap film (4). Concurrently with our research, other researchers have also investigated the combustion products of PVC polymers and plastics, and this report includes not only our own findings but a review of selected data published by others.

As many as seventy-five compounds (5), mainly aromatic and aliphatic hydrocarbons, have been identified as products of combustion of polyvinyl chloride. From the polymer itself no oxygenated compounds have been reported (except CO and CO₂) even when burned in air, but a few such compounds (6, 7, 11) can be found in the formulated plastics, probably originating from the plasticizer or other additives. The types of combustion used in the laboratory studies have varied considerably, both in temperature and in the amount of air used. In the latter case, some experiments have been carried out in a completely inert atmosphere (5, 6, 9, 12), while in others, air (3, 5, 7, 8) and oxygen-enriched air (3) have been used. Likewise, the temperatures have varied from as low as 100°C (9) up to the temperatures of an electric arc (10). Generally though, the temperatures have ranged from 250°C, where the dehydrochlorination becomes measurable, to 600°C, where most formulations of PVC will be totally consumed. For heating up to 600°C, a tubular combustion furnace is frequently used with a combustion tube of quartz or Vycor. This provides a chamber that is resistant to the chemical action of the combustion gases and permits the displacement of these gases by

flowing controlled amounts of air or other gases through the tube. In our work, we generally used a flow of about 0.1 - 1.0 liters per minute. Others have used hot plates or open cone heaters within a closed chamber, such as the NBS Smoke Chamber. The rates of heating have varied from a steadily increasing programmed rate (3, 8) up to instantaneous heating (5, 6, 7, 9, 12).

PRODUCTS TESTED

The types of PVC tested fall into two categories, i.e. the polymer itself, and plastic formulations. In the few reports where this information is available, the polymers varied in molecular weight from 45,000 to 250,000. The plastic formulations tested vary considerably, including those intended for wire insulation, floor tile, and other construction uses; but generally contain a plasticizer and other fillers to optimize the product for its particular usage. The amounts of polymer vary from 30 to 60% in the plastic formulations.

QUALITATIVE ANALYSIS

In our research we were primarily concerned with the "volatile products" of combustion, and therefor optimized collection and analytical techniques for such compounds. As a result, we found 59 compounds (3), 52 of which were identified. Woolley (5) made a more extensive collection, using a liquid nitrogen trap, and as a result found 75 compounds, identifying 21 of these in his publication. His chromatographic peak No. 49 was identified as *o*-xylene, the highest boiling compound we collected, and it appears that the additional compounds found are those less volatile than the xylenes. He identified his peak No. 75 as naphthalene.

The principal products of combustion of PVC polymers are hydrogen chloride, carbon dioxide, carbon monoxide, and water. The organic products formed are principally aliphatic and aromatic hydrocarbons, with benzene predominating. Only very small amounts of two chlorinated compounds were found, i.e. methyl and vinyl chloride. None of the identified products were oxygenated compounds, except for carbon dioxide and carbon monoxide, indicating that the breakdown process is non-oxidative (3, 5).

The compounds reported in our earlier work were present in both the polymers and the plastic formulations, with the indication that they originated primarily from the polymer, and it was postulated at that time that additives contribute mostly to higher boiling combustion products. Since then we have worked with PVC food-wrap films, and in these plastics have found both unmodified plasticizer and traces of acrolein and styrene. O'Hara (6) compared the high temperature (600°C) pyrolysis (in helium) of a PVC polymer with a plastic containing 63% of the polymer and 37% of *o*-dioctyl phthalate. He found products characteristic of both the PVC and the phthalate plasticizer, but no products resulting from the interaction of the two.

QUANTITATIVE ANALYSIS

Quantitative determinations in our research were carried out on twenty-two compounds, selected on the basis of their quantity or environmental concern. Of greatest importance are hydrogen chloride, carbon monoxide, benzene, toluene, vinyl chloride, phosgene and benzyl chloride. The amounts of twelve of these compounds are tabulated in Table I for two combinations of polymer and plastic. Plastic G contains 51% of polymer B and plastic E contains 57% of polymer C. It will be noted that the aliphatic compounds in the plastics have all increased in quantity by factors ranging from 1.2 to 6.1 times that in the polymer, although the amount of polymer has decreased. Two points should be made regarding the vinyl chloride concentrations shown. First, the increase in vinyl chloride from the plastics may not be real, as it has been determined that acetaldehyde (a combustion product of the plasticizer) co-elutes on the chromatographic column used. Second, although we believe a portion of the vinyl chloride reported actually results from thermal degradation, the residual monomer may have been higher in the PVC produced in the 1960's than in present-day PVC.

CHANGE IN PRODUCTS WITH TEMPERATURE

It has long been known that the decomposition of PVC begins with dehydrochlorination, with this process taking place in a narrow temperature range around 280°C. Thermogravimetric analysis shows the process beginning in measurable quantities at about 250°C and being completed by 300°C. The 60% weight loss of the polymer up to 300°C has been shown by collecting and analyzing the combustion gases to be almost entirely due to the formation of hydrogen chloride (and a small amount of benzene), and this accounts for almost all the chlorine in the polymer. The same is the case for plastics, where the hydrogen chloride represents almost all of the chlorine in the polymer used in the formulation. In some cases however, where the formulations contain reactive inorganic compounds, the amount of hydrogen chloride

TABLE 1. Comparison of combustion products of two plastics with the combustion products of their polymers

Compound	Combustion products, mg/g			
	Polymer B*	Plastic G	Polymer C	Plastic E
HCl	583.	273.	584.	333.
CO	442.	67.	403.	90.
Methane	4.6	6.6	5.8	6.8
Ethylene	0.58	2.3	0.33	2.0
Ethane	2.2	3.0	2.5	2.9
Propylene	0.47	2.0	0.56	1.4
Propane	0.84	1.7	1.1	1.4
Vinyl chloride	0.60	3.3	0.52	2.6
1-Butene	0.18	1.1	0.28	0.58
Butane	0.28	1.1	0.39	0.74
Benzene	36.	10.	29.	11.
Toluene	1.3	0.94	1.1	1.0

* see Reference 3.

measured is less than the amount liberated from the polymer. Chang and Salovey (12), in studying the thermal degradation of PVC in an inert atmosphere, reported a greater temperature range for HCl evolution. They stated that the liberation of this gas begins at about 200°C and the rate increases to reach a maximum at 340°C. Woolley (5) measured the release of HCl as 94% and 96% of theoretical in nitrogen and in air, respectively, at 300°C. Liebman, et al. (8) determined that the maximum rate of weight loss for the dehydrochlorination process was at 290°C in air and at a slightly higher temperature in nitrogen.

The other major product evolved in heating to 300°C is benzene. This compound is the predominant organic in the thermal degradation of PVC polymer, with 25 to 50 mg per gram of polymer formed in burning up to 600°C (see Table 2). Most of this benzene is evolved before 300°C along with the hydrogen chloride. The maximum generation of the other hydrocarbons takes place between 350° and 450°C, with the quantities generally less than 1.0 mg per gram of polymer.

CHANGES IN PRODUCTS WITH VARYING AIR SUPPLY

The types of thermal degradation or combustion used by various investigators have varied from a complete absence of oxygen to air with added oxygen. This does not change the number or types of products formed and, except for CO₂ and CO, does not change the quantities appreciably. The amounts of HCl and benzene generated do not change, and their temperature of evolution changes only slightly. However, Woolley (5) has shown that the rate at which hydrogen chloride is released increases with increasing amounts of air.

In our experiments where we varied the amount of air available when burning a polymer (3), it was found that all of the hydrocarbons other than benzene and vinyl chloride decrease with increasing air. Benzene remained constant while vinyl chloride increased slightly.

TABLE 2. Variation of combustion products of Polymer A* with Temperature

Compound	Combustion products, mg/g				
	25- 280°C	280- 350°C	350- 430°C	430- 510°C	510- 520°C
CO ₂	---	9.7	181.	244.	237.
CO	---	20.	46.	151.	181.
Methane	---	0.20	1.3	1.8	0.31
Ethylene	0.04	0.33	0.39	---	---
Ethane	---	0.12	0.94	0.41	---
Propylene	0.06	0.11	0.31	---	---
Propane	---	0.08	0.44	0.11	---
Vinyl chloride	0.04	0.25	0.17	0.02	---
1-Butene	0.02	0.04	0.08	---	---
Butane	---	0.03	0.20	0.02	---
Isopentane	---	---	0.005	0.001	---
1-Pentene	---	0.01	0.03	---	---
Pentane	---	0.01	0.08	0.01	---
Cyclopentene	---	0.02	0.01	---	---
Cyclopentane	---	0.01	0.02	---	---
1-Hexene	---	0.01	0.02	---	---
Hexane	---	0.01	0.05	0.01	---
Methylcyclopentane	---	---	0.02	---	---
Benzene	24.	6.6	0.35	0.16	---
Toluene	0.12	0.18	0.55	0.03	0.01

* see Reference 3.

PHOSGENE: A PRODUCT OF COMBUSTION?

For years, it has been claimed by some that phosgene is one of the products of thermal degradation or combustion of PVC. This claim has been very popular with the press and fire investigators when reporting on fires involving furnishings and insulation containing this polymer. In some cases, it has been suggested that this compound contributed to the deaths of people killed by the toxic fumes of a fire. Although researchers who have been concerned with the identification of the products of combustion of PVC have attempted to identify phosgene, they have not generally been successful. Coleman and Thomas (14) have reported finding small amounts (up to 10 ppm), but others, although stating that they have attempted to find it, have been unsuccessful (3, 5, 11, 13). The limits of detection have varied from 0.1 ppm to 50 ppm.

Recently, Brown and Birky (10) have published results from a study to determine whether phosgene is a thermal decomposition product of PVC where electrical fires are the source of combustion. Four methods of decomposition were studied: (1) thermal degradation of PVC in a resistively heated furnace, (2) electrical overloading of a PVC clad wire, (3) electrical arcing between electrodes partially covered with PVC, and (4) electric arc initiated flaming combustion in a cup furnace. Results are reported which show that yields of 0.2 to 1.6 mg of phosgene can be generated per gram of PVC by the electric arc decomposition. Lesser amounts (0.1 to 0.2 mg/gm) were found in the other types of combustion. The identification and quantitation of phosgene in the decomposition products were obtained through the use of gas chromatography, infrared spectroscopy and mass spectrometry.

PVC FOOD-WRAPPING FILMS

Since 1973, there has been an interest in the combustion products formed in cutting clear plasticized PVC film used to package meats and other food products in supermarkets. At that time, an occupational health problem, labelled "meat wrappers asthma" was described

(15), with the suggestion that the source of the problem was the thermal decomposition products resulting from the hot-wire cutting of these food-wrap films. The film, which is about 0.2 mm thick, is thermally cut for each package from a roll using either a 0.5 mm diameter hot-wire (200° to 350°C) or a 10 mm diameter "cool rod" (135°C). The portion of the film, in contact with the wire or rod during cutting may be subject to thermal degradation and/or volatilization of film components. We carried out a study to determine what compounds were generated and released in this cutting operation, and found that more than sixteen compounds were liberated, most in extremely small quantities. The types of films tested, the method of containing and collecting the evolved compounds, and the analytical procedures used are described in Reference 4.

The principal products which were determined quantitatively were hydrogen chloride, plasticizer, benzene, toluene, acrolein, and carbon monoxide. Benzyl chloride was not found in the products involved. Its presence had been reported by Vandervort (16) when heating plasticized film to 230°C in an all-glass vessel. However, using gaseous and liquid benzyl chloride standards and the hot-wire cutting device, we found that benzyl chloride could not be recovered either in the gas phase or in a concentrated hood wash. The decomposition of this compound in the presence of hot iron may account for its absence. Compounds analyzed and normal concentration ranges found included hydrogen chloride (1-10 µg per cut), plasticizer (1-50 µg per cut), benzene and toluene (each <5-20 ng per cut), acrolein (25-150 ng per cut), and carbon monoxide (2-4 µg per cut) using the hot wire. Room air samples, collected during the hot-wire cutting without the sampling hood, had less than 0.25 ppm hydrogen chloride. Using the cool-rod cutting device hydrogen chloride, benzene, and toluene were not detected. Plasticizer was detected (25-86 µg per cut) using the cool rod.

CONCLUSIONS

On the basis of what is known about the toxicity of the individual products of combustion, and the amounts of these products as determined experimentally by our research and that of others, we have concluded that by far the greatest hazard associated with exposure to burning PVC is that stemming from the evolved hydrogen chloride and carbon monoxide. This conclusion does not take into account any possible synergistic effect of other compounds in combination with the two principal products, but toxicity studies to date have not yet established such interactions.

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