

Vinyl chloride

Combustion Products from Vinyl Chloride Monomer

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By means of a variety of analytical techniques, the combustion profile of vinyl chloride monomer (VCM) has been determined. This profile includes flame temperatures, soot content, and a combustion gas analysis. Depending on the amount of VCM-air premixing prior to combustion, the temperature of a VCM flame ranges from 950° to 1466°C. Similarly, the soot or unburned carbon content of a VCM flame varies from 3 to 6 weight percent. An analysis of the combustion gases from VCM reveal the following composition: HCl 27,000 ppm; CO¹ 58,100 ppm; CO 9500 ppm; phosgene 40 ppm; and VCM trace. From a hazard standpoint, the gross quantity of hydrogen chloride is the main source of danger in a VCM fire.

Introduction

THE COMBUSTION PRODUCTS from chlorinated hydrocarbons are of considerable importance from a toxicological standpoint. This class of organic compounds, when burned or thermally degraded in an oxidizing atmosphere, can produce carbon monoxide, hydrogen chloride, and phosgene. The highly chlorinated hydrocarbons (carbon tetrachloride, etc.) have been well characterized in this respect. For example, Sjöberg¹ has determined the amount of phosgene and hydrogen chloride released from a series of chlorinated hydrocarbons when brought into contact with hot metal surfaces, glowing charcoal, and an open flame. The results of this study showed that, at temperatures above 600°C, the major combustion product was hydrogen chloride.

In a more recent study Jay² has found that, at decomposition temperatures between 600° to 700°C, the presence of phosgene from chlorinated hydrocarbons was noted only when the following empirical ratio (α) for the

molecule was greater than or equal to 0.40:

$$\alpha = \frac{(\text{No. of Cl atoms}) - (\text{No. of H atoms})}{(\text{No. of C atoms})}$$

Little has been reported in the literature on comparable studies involving the combustion of vinyl chloride monomer (VCM). Kubler³ has analyzed the combustion products from a number of halogenated aerosol propellants and has reported that, in a hot flame at 1000°C, 100 gm of VCM will generate the following levels (for a room having a 50-m³ volume): CO 63.2 ppm; COCl₂ 0.05 ppm; and HCl 126 ppm. Under these specific conditions, HCl would seem to contribute the greatest to the overall toxicity of the combustion products. (Recent work on the toxicity of the combustion products from polyvinyl chloride has shown that carbon monoxide and not HCl is of major toxicological importance under some conditions.⁴)

Current interest in the combustion products from large amounts of VCM has prompted the present study. Kubler's results on the combustion of VCM is of limited use in this respect owing to the fact that, in his study, VCM was decomposed in an external fire. Our interest was in the self-ignition and combustion of VCM in the absence of an external fuel. In this respect, we have determined the

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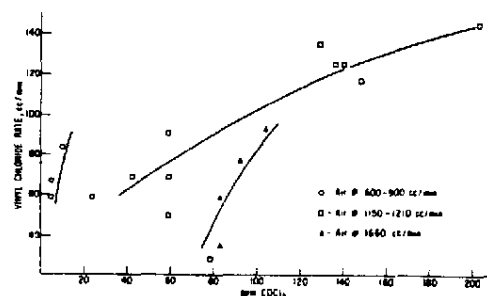


FIGURE 1. Effect of feed composition and burning rate on phosgene production.

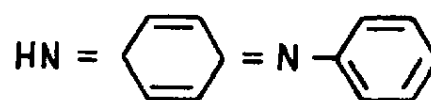
combustion products from VCM under both diffusion and premixed flame conditions. The temperature of the flame and the amount of soot generated in a VCM flame was also measured.

Phosgene Determinations

Linch *et al.*⁵ have reviewed a number of methods for carrying out an analysis of phosgene in air. Many of the colorimetric methods listed are so sensitive to HCl that they were of little use in the current study. While attempting to determine phosgene in a VCM flame with the colorimetric detector 4,4-bis-(diethylamino)benzophenone, we found that the combustion gases from VCM convert this reagent to a form (probably the HCl salt) that is totally insensitive to pure phosgene.

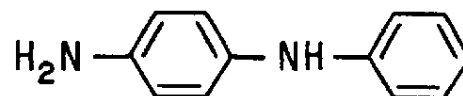
Phosgene analyses by the aniline method described by Crummett⁶ were also attempted. In this method, the combustion gases were scrubbed in an aqueous aniline trap; any phosgene present is converted into 1,3-diphenylurea which then can be determined spectrophotometrically. In carrying out this analysis, we found that, when the combustion products from VCM were directed into this solution, a precipitate was formed. The ultraviolet spectrum of this material in methanol exhibited an absorption at 254.5 mμ, indicating it to be 1,3-diphenylurea. The mass spectrum of this material, however, unequivocally showed that not even trace amounts of 1,3-diphenylurea were present. Rather the composition of this precipitate consisted of materials that result from the

oxidative coupling of aniline. We have identified the following components:



M/E = 182

and



M/E = 184

and polymeric forms thereof.

The high level of HCl in the combustion gases is the cause of this oxidative coupling of aniline. Indeed, aniline can only undergo oxidation when present in the form of a salt (that is, aniline hydrochloride).⁷ Additional evidence further points up the inadequacy of the aniline method for determining phosgene in the presence of large amounts of HCl. It has been shown that the conversion of phosgene to 1,3-diphenylurea is pH-sensitive and that, at pH = 1.97, the efficiency of this reaction is only 9.3%.⁸

To circumvent these problems, a gas chromatographic analysis of the combustion gases, aimed at determining phosgene, was devised. For this particular analysis, either of two chromatographic columns was used. Chromatographic conditions are summarized in Table I. In addition to these analyses, phosgene determinations were also carried out with a Model 21/31 Drager multi-gas detector equipped with CH283 Drager tubes.

Phosgene analyses were made on VCM flames under a number of experimental conditions. The following flames were probed: microburner, copper tubing burner containing VCM and air feed lines, glass tubing burner, VCM burning in a watch glass and VCM burning in a ruptured 1-liter metal cylinder. In each case, low levels (15 to 150 ppm) of phosgene were detected. Extensive data collected, using the all-glass burner, indicate that an optimum air/VCM ratio is required for the production of phosgene; ratios above or below this optimum tend to

TABLE I
Gas Chromatographic Conditions
for Phosgene Determination

Safflower oil column:	15 % safflower oil on 30/60 CHR W, non a.w.; 12' X 1/8" copper column; detector, t.e., 36°C carrier gas, helium, 40 cc/min.
Silicone oil column:	20% Dow Corning silicone oil 703 on 60/80 CHR W, non a.w.; 12' X 1/8" copper column; detector, thermal conductivity, 58°C; carrier gas, helium, 94 cc/min.

TABLE II
Chromatographic Parameters for
CO and CO₂ Analysis

Porapak column:	6' X 1/8" s.s. Porapak S, 80/100 mesh; detector, thermal conductivity, carrier gas: helium
Molecular sieve:	1' X 1/8" s.s. molecular sieve 5A, 45/60 mesh; all other chromatographic parameters identical to above (see text for further information)

suppress phosgene formation. The relationship of the rate of feed of VCM to the burner, the rate of air feed, and the amount of phosgene produced is illustrated in Figure 1.

Air samples above a watch glass and above a ruptured metal tank containing burning VCM were collected and analyzed for phosgene. These samples were of special significance in that they simulated actual burning conditions. The air sample obtained above the watch glass contained 15 to 20 ppm of phosgene, and that above the ruptured metal cylinder contained 40 ppm of phosgene.

The Drager detector was insensitive to phosgene in these experiments due to the high level of HCl in the combustion gases. However, this problem was easily circumvented by attaching an HCl scrubber to the tube. This scrubber consisted of a small section of glass tubing containing 20-mesh granular zinc. The Drager tube values varied $\pm 25\%$ from the gas chromatographic values. The Drager tube when equipped with the zinc scrubber would be a valuable monitoring device for use at the site of a vinyl chloride fire.

VCM Flame Temperature

The temperature of a vinyl chloride flame was measured under diffusion and premixed conditions. Under diffusion conditions, only VCM was fed to the burner (65 to 90 cc/

min). Ambient air was the only source of oxygen. For a premixed flame, air (120 to 190 cc/min) and VCM (65 to 90 cc/min) were both fed to the flame; ambient air was also available to sustain combustion. Temperature measurements were made with a Platinel[®] thermocouple (0.008 inch in diameter). For a VCM diffusion flame, the highest temperature recorded was 950°C, while for a premixed flame, the highest temperature recorded was 1466°C. The diffusion flame best simulates an actual VCM fire in that there is little premixing of air and VCM in the pre-ignition step of a flame.

The fact that a VCM fire has a characteristic "cold" flame is evident from the amount of soot generated. From a number of experiments on VCM diffusion flames, it appears that the amount of soot produced during combustion ranges from 3 to 6% of the VCM consumed. This range corresponds to 7 to 15% of the available carbon in the VCM molecule.

HCl from Burning VCM

Initial studies with phosgene determinations indicated that the combustion gases from VCM contained a high level of HCl. In order to better quantify this value, the combustion gases from a VCM flame were directed into a standardized NaOH solution. Back titration of this solution afforded the quantity of HCl produced during VCM combustion. In terms of the amount of VCM burned, this level of HCl is approximately 52%. Although a theoretical yield of 58% is expected, the above analysis did not account for the HCl lost on the walls of the combustion apparatus or for the VCM that escaped combustion.

CO/CO₂ in VCM Combustion Gases

This analysis was carried out through the use of two chromatographic columns. (Column parameters are summarized in Table II). Briefly, the separation is achieved by placing a 6-foot Porapak S in series with a 1-foot 5A molecular sieve column. The air sample is injected into this two-column system: after elution of oxygen, the sieve column which contains the nitrogen and CO com-

TABLE III
CO/CO₂ Analysis of VCM Combustion Gases

Component	Volume %
O ₂	14.71
CO ₂	5.81
N ₂	78.53
CO	0.95

ponents is isolated by means of a 6-port valve. The Porapak column is then heated to 245°C, resulting in the elution of CO₂, ethylene, and VCM. On completion of this analysis, the molecular sieve column is put back in series and heated until the CO and N₂ elute. In this way, a complete separation and analysis of CO, CO₂, N₂ and O₂ are obtained. Response factors were obtained for each of these components so that the analysis could be expressed on a volume basis.

Air samples were also obtained above a VCM diffusion flame; Table III contains a summary of a typical analysis. It should be noted that this analysis has not been corrected for HCl or combustion water content. It is also recognized that the results of each of these analyses (except the HCl analysis) are dependent on the actual conditions employed. For example, the relative levels of phosgene, CO, and CO₂ would be different in a fire where oxygen depletion is a factor. However, oxygen depletion would tend to suppress the formation of COCl₂ and CO, so the values cited herein represent near maximum concentrations.

Total Combustion Analysis

The various analyses cited in this paper can be combined to give an overall combustion profile for VCM. Based on the CO/CO₂ and phosgene gas analyses and on the hydrogen chloride determination (52% of the monomer), an approximate analysis of an air sample obtained immediately above a VCM flame would be, in ppm): HCl 27,000 ppm;

CO₂ 58,100 ppm; CO 9,500 ppm; phosgene 40 ppm; and VCM trace.

Conclusions

It is felt that, from a hazard standpoint, the gross quantity of HCl in the combustion gases from VCM is the main source of danger. While it is recognized that, in the very near vicinity of a VCM fire, dangerous amounts of phosgene may be present, it is noted that at this point the atmosphere will already have been rendered insupportable by the high concentration of HCl.

The pungent odor of HCl would also act as a warning device to clear the area or to obtain the necessary breathing apparatus to deal with the fire.

Acknowledgments

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