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ISSN: 0973-4945; CODEN ECJHAO
E-Journal of Chemistry
2009, 6(3), 685-692

Determination of HCl and VOC Emission from Thermal Degradation of PVC in the Absence and Presence of Copper, Copper(II) Oxide and Copper(II) Chloride

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Received 20 January 2008; Revised 20 June 2008; Accepted 26 December 2008

Abstract: Polyvinyl chloride (PVC) has played a key role in the development of the plastic industry over the past 40 years. Thermal degradation of PVC leads to formation of many toxic pollutants such as HCl, aromatic and volatile organic carbon vapors. Thermal degradation of PVC and PVC in the presence of copper, cupric oxide and copper(II) chloride were investigated in this study using a laboratory scale electrical furnace. HCl and Cl⁻ ion were analyzed by a Dionex ion chromatograph and VOCs compounds were analyzed using GC or GC-MS. The results showed that HCl plus Cl⁻ ion and benzene formed about 99% and 80% respectively in the first step of thermal degradation under air atmosphere. The presence of cupric oxide increases the percentage of short chain hydrocarbons more than 184% and decreases the amount of the major aromatic hydrocarbon and HCl plus Cl⁻ ion to 90% and 65% respectively. The total aromatic hydrocarbon emitted less than when atmosphere was air and difference was statistically significant ($P_{\text{value}} < 0.000$).

Keywords: Polyvinyl chloride, Thermal degradation, VOC, Harmful emission

Introduction

The incineration of municipal solid wastes has become an alternative to the practice of dumping refuse in landfill sites^{1,2}. Incinerating of wastes in plants close to urban areas offers the advantages of low transportation costs, reduction in the volume of solid wastes and the possibility of energy recovery³. In general, the uncontrolled incineration of refuse, and combustion processes emit potentially hazardous substances into the environment, especially

into the atmosphere^{1,4,6}. Jay *et al.* identified 250 individual organic compounds at concentrations above 50 ng/m³ in the emission of incinerator⁷. Common uses for PVC are in the construction and plumbing industries and in some food, shampoo, and household product containers.

It is well known, hydrochloric acid (HCl) is a major toxic emission during incinerating of chlorinated plastic⁸⁻¹⁰. The first step of PVC thermal decomposition is dehydrochlorination and loss of HCl leaves some residue of polyene that can yield a vast array of hydrocarbon products undergo further pyrolysis.

Our primary objective in this study was to measure some harmful volatile and semi-volatile emission from combustion and pyrolysis of PVC in the absence of additive and in the present of some copper compounds.

Experimental

PVC was supplied from Aldrich chemical Co. Copper compounds of AR grade were obtained from BDH Ltd. For determination of HCl plus Cl⁻, 2 mg of pure PVC or mixture of PVC with copper, cupric oxide or copper(II) chloride were heated in an electric furnace. The samples were placed in a silica crucible and introduced into the furnace. The temperature was preset to final temperature at a rate of 10 °C per minute. The weight of the copper compounds used through this work was 10% of the weight of PVC. For determination of HCl plus Cl⁻ the sampling time was either the same as the combustion time or combustion time plus 15 and 30 minutes. HCl has high solubility in water therefore water has usually been used as absorbent in the sampling bubbler or impinger. The collection efficiency of chloride in water is, however, very low and for this reason adsorption solution was the same as chromatographic eluent that is 0.00075 M NaHCO₃ + 0.0022 M Na₂CO₃. HCl and chloride ion emitted were bubbled through a bubbler containing 30 mL of the absorption solution and then through a fritted bubbler contained the same solution. The flow rate was 0.75 liter per minute in the duration of sampling time. The solution was analyzed for chloride ion and HCl by ion chromatography. A Dionex ion chromatograph Model 2010I with a conductivity detector was used for analysis of chloride ion and hydrogen chloride. A column HPLC-AS4A and a guard AG4A were used with 0.025N sulfuric acid as suppressor at flow rate of 2.5 cm³/min. Before introducing the samples to HPLC, samples are filtered with an acid free filter paper to separate particulates and oily compounds.

The sampling of short chain hydrocarbons was achieved by passing the flue gas stream through a cooling trap and then drawn through a 37 mm fiber glass filter before collection in a Tedlar sampling bag using a small personal pump. The sampling flow rate was controlled to obtain a constant at 30 mL/min. A Pye Unicam PU 4500 Gas Chromatograph was used for determination of short chain linear gases. The GC temperature was held for 4 minutes at 50 °C then increased at rate 16 °C per minute to 200 °C, where the temperature was held for 10 minutes. A one meter packed column containing 60-80 mesh chromosorb 102 and flame ionization detector at 200 °C were used. The carrier gas was nitrogen with a head pressure of 0.55 kg/cm².

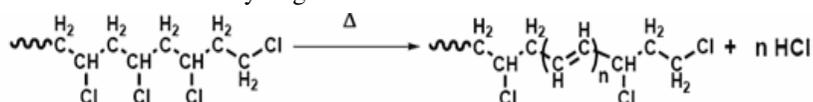
For the determination of Dioxin, about 100 mg sample of pure PVC and the same ratio of PVC with copper compounds were burnt under the same temperature conditions and for other chlorinated aromatic or aromatic hydrocarbons 2 mg Pure PVC or mixture of PVC and copper, copper(II) chloride or cupric oxide were introduced to furnaces. For sampling of chlorinated aromatic hydrocarbons, aromatic hydrocarbons and some volatile hydrocarbons a

Supelco Carbotrap 300 with a gas flow rate of 35 mL per minute for 12 min was used. This carbotrap is a multi-bed trap and contains the absorbent carbotrap C, carbotrap B and carbosieve S-III. A 37 mm diameter fiber glass filter paper was used for sampling of aromatic and chlorinated aromatic hydrocarbons aerosols in this work. After sampling the filter paper was cutted and placed into a 4 mm ID glass tube and introduced to thermal desorption extraction of compounds. A conditioned Supelco Carbotrap 150 with a sampling flow rate of 50 mL/min for 15 minute was used for determination of dioxin. For determination of 2,3,7,8 TCDD aerosols a 37 mm diameter fiber glass paper was used and the filter holder was held in 170 °C. The thermal desorption method was used as a direct extraction method to introduce analyte to GC-MS for an on-line analysis. Supelco fused silica capillary columns 30 m x 2.5 mm x 2.5 µm and 60 m x 0.25 mm x 0.2 µm were used for analysis of aromatic, chlorinated aromatic hydrocarbons and for dioxin respectively. The GC temperature was held 5 min at 30 °C and then increased at rate 5 °C per minute to 200 °C to determine of aromatic and chlorinated aromatic hydrocarbons and some volatile compounds concentration. To determine of 2,3,7,8 TCDD concentrations, temperature was held 1 min at 200 °C and then rising to 260 °C at 8 °C/min and was held there for 20 min. The mass spectrometer was used as detector that was operated in the ion selective mode for identification of 2,3,7,8 TCDD at a minimum; ions 322 and 323 are used.

Results and Discussion

Table 1 shows the concentration of Cl⁻ ion plus HCl in the gaseous emissions from combustion of samples in air at temperatures up to 600 °C. The results show the concentration of Cl⁻ ion plus HCl increases with increasing temperature and combustion time. The level of Cl⁻ ion plus HCl in the gashouse emissions from PVC in the presence of CuO was less than other mixtures of PVC (6500 ppm) while the emissions from PVC in the presence of CuCl₂ were the highest (11825 ppm). The emission of hydrogen chloride from PVC is generally observed at a relatively low temperature. Dechlorination is almost complete at ~ 350 °C, however, some further HCl formation was also found at a higher temperature^{11,12}. Blazso *et al* showed that dehydrochlorination and benzene formation take place at a lower temperature and the apparent rate of these reactions decreases in the presence of iron oxide and iron oxide has a strong accelerating on the dehydrochlorination of PVC¹³. Marongiu *et al.* showed that dehydrochlorination was happen in the first step of thermal degradation¹⁴. Table 2 shows the concentration of Cl⁻ ion plus HCl in gashouse emissions from samples heated in an atmosphere of nitrogen at temperatures up to 600 °C. The levels of Cl⁻ ion plus HCl in the presence of CuO and copper are 6500, 8250 ppm in air and 8500, 9045 ppm in an atmosphere of nitrogen respectively. The results show that concentration of Cl⁻ ion plus HCl from combustion of PVC in the presence of CuO and copper in air are less than that in an atmosphere of nitrogen. The C-Cl bonds are loosed due to the reaction of the chlorine ion with the metal; chlorine driven away from the carbon atom reaches more easily hydrogen to form HCl at alower temperature than without the interaction of the metal¹³. Karavidirim and *et al.* showed that dehydrochlorination of PVC was accelerated¹⁵ in the presence of FeCl₃.

The scheme 1 shows the hydrogen chloride elimination of PVC.



Scheme 1. Hydrogen chloride elimination.

Table 1. Concentration of Cl plus HCl in gas emission from the combustion of sample in air.

Sample	Temperature °C	Con. on reaching final temperature ppm	Con. after 15 min at final temp. ppm	Con. after 30 min at final temp. ppm
PVC	250	190	2250	5560
PVC	340	4500	9900	10000
PVC	600	-	10950	-
PVC + CuCl ₂	100	45	96	112
PVC + CuCl ₂	340	7825	9700	10750
PVC + CuCl ₂	600	-	11825	-
PVC + CuO	290	1175	5000	6000
PVC + CuO	370	3850	5700	5800
PVC + CuO	600	-	6500	-
PVC + Cu	270	900	4550	7500
PVC + Cu	380	5100	6925	7700
PVC + Cu	600	-	8250	-

Table 2. Concentration of Cl plus HCl in gas emission from the combustion of sample in nitrogen.

Sample	Temperature °C	Con. on reaching final temperature, ppm	Con. after 15 min at final temp. ppm	Con. after 30 min at final temp. ppm
PVC	250	180	2050	5075
PVC	340	4400	9700	9750
PVC	600	-	10600	-
PVC + CuCl ₂	100	43	92	105
PVC + CuCl ₂	340	7950	9275	9000
PVC + CuCl ₂	600	-	9900	-
PVC + CuO	290	1225	6500	8125
PVC + CuO	370	5475	8100	8250
PVC + CuO	600	-	8500	-
PVC + Cu	270	1000	5275	8425
PVC + Cu	380	5825	7900	8500
PVC + Cu	600	-	9045	-

Table 3 shows the concentration of methane, ethylene, ethane, propylene, propane and *n*-butylene in the gaseous products from pyrolysis of PVC alone and PVC in the presence of copper, cupric oxide and copper(II) chloride in an atmosphere of nitrogen. It is clear that the largest concentrations of methane and ethylene are observed in the presence of cupric oxide which are 27000 and 8700 ppm respectively. Also the data shows the concentrations of short chain gashouse products in the presence of CuO, CuCl₂ and copper are higher than that from the pyrolysis of PVC alone. Table 4 contains data on the level of short chain linear gashouse products in the combustion of PVC alone and in the presence of copper, copper(II) chloride and cupric oxide. It is clear that the combustion of PVC in the presence of CuO, CuCl₂ and copper generates more short chain gases than does PVC alone and the combustion of PVC in the presence of CuO produces more methane and ethane which are 27500 and 12200 ppm respectively.

Table 3. Concentration (ppm) of short chain gases produced by the pyrolysis of PVC alone and in the presence of some copper compounds under nitrogen.

Sample	Methane	Ethylene	Ethane	Propylene	Propane	<i>n</i> -Butylene
PVC	13500	1600	3800	1400	200	800
PVC+CuO	27000	8700	7925	3425	1000	6700
PVC+CuCl ₂	20500	5000	10600	4000	1800	6700
PVC+Cu	13000	1200	6500	1400	1050	2700

Table 4. Concentration (ppm) of short chain linear gases produced by the combustion of PVC alone and in the presence of some copper compounds under air.

Sample	Methane	Ethylene	Ethane	Propylene	Propane	<i>n</i> -Butylene
PVC	17000	4300	5520	1250	600	3050
PVC+CuO	27500	5600	12200	3000	2400	7800
PVC+CuCl ₂	18300	4300	12000	2050	2100	6000
PVC+Cu	25200	7200	10100	3900	1900	12100

Table 5. The amount (μg) of organic gases products from the combustion of pure PVC and mixture of PVC in the presence of copper, copper(II) chloride and cupric oxide at 300 °C under air.

Product	PVC	PVC +Cu	PVC + CuCl ₂	PVC + CuO
Benzene	440	410	40	37
Toluene	11	4.1	3.2	2.1
<i>o</i> -Xylene	-	-	-	-
Naphtalene	-	-	-	-
Chlorobenzene	2	2.1	0.008	0.003
Ethyl benzene	1	-	-	-
<i>p</i> -Dichlorobenzene	-	0.008	0.003	0.001
<i>o</i> -Dichlorobenzene	0.07	0.012	0.0007	0.0002
1,2,5- Trichlorobenzene	-	-	-	-
1,2,4- Trichlorobenzene	0.09	-	-	-
1,2,4,5- Tetrachlorobenzene	0.03	0.045	0.0009	0.0005
Pentachlorobenzene	0.01	0.023	-	-
Hexachlorobenzene	0.03	0.08	-	-
2,3,7,8-TCDD	15ng	46ng	40ng	32ng
Tetrachloroethylene	1.01	1.03	1.2	2

Table 5 shows a list of the organic products identified from the combustion of pure PVC and PVC in the presence of copper, copper(II) chloride and cupric oxide at 300 °C in air. The results show that benzene is the major aromatic product that it is 440 micrograms in combustion of PVC alone. The concentrations of benzene, toluene and some chlorinated aromatic hydrocarbon decrease in the combustion of PVC in the presence of CuO. Benzene, toluene, and further poly aromatic hydrocarbons are recognized as the volatile products of the thermal decomposition of polyenes. The formation of aromatic products was proved to undergo intermolecular cyclic reactions¹⁶. The formation of benzene from PVC involves not only the elimination of at least three HCl from a segment of six carbon atoms, but also the detachment of

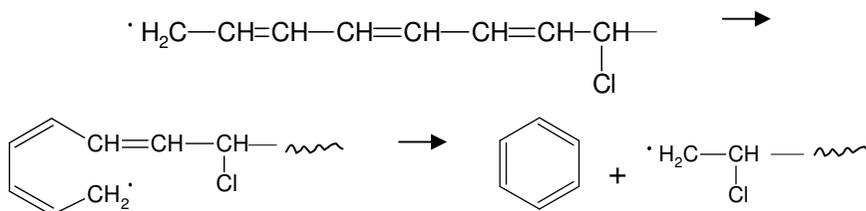
performed cyclohexadiene moiety out of the polymer chain. The concentration of 2,3,7,8 TCDD however, increases when PVC was burned in the presence of copper and copper compound. The cyclization reaction would occur by a depropagation process, with subsequent splitting off benzene and regeneration of the radical¹⁸. Table 6 demonstrated a list of the products of combustion of pure PVC and of mixture of PVC with copper, copper(II) chloride and cupric oxide at 600 °C. The results show that formation of aromatic hydrocarbons decrease when combustion is carried out in the presence of the copper compounds. Grimes *et al.* reported that thermal degradation of PVC in air in nitrogen in the presences of Cu, CuO, and CuCl₂ can decrease the percentages of volatile products¹⁷. There are two possible mechanism which Those could be achieved (1) the CuCl₂ formed in the process is a Lewis acid and therefore can affects on the nature of the reaction in the system, thus suppressing the formation of the precursor to the aromatic molecules and at the same time providing more aliphatic fragment (2) Cu and CuO could catalyze either or both of the following reaction.

- Cross linking by free radical reaction
- Reaction at double bonds

Table 6. The amount (µg) of organic gases products from the combustion of pure PVC and mixtures of PVC in presence of copper, copper(II) chloride and cupric oxide at 600 °C under air.

Product	PVC	PVC +Cu	PVC + CuCl ₂	PVC + CuO
Benzene	500	410	80	45
Toluene	68	54	33	2.0
<i>o</i> -Xylene	0.9	0.8	0.32	0.2
Naphtalene	3.65	2.9	0.42	0.255
Chlorobenzene	1.22	1.27	0.9	0.7
Ethyl benzene	4.05	4	3.1	2.8
<i>p</i> -Dichlorobenzene	0.35	0.5	0.12	0.08
<i>o</i> -Dichlorobenzene	8.56	9.1	2.3	1.8
1,2,5- Trichlorobenzene	1.2	1.1	9.1	0.62
1,2,4- Trichlorobenzene	5	6.1	2.5	2
1,2,4,5- Tetrachlorobenzene	6.2	7.8	3.1	2.2
Pentachlorobenzene	3.8	4.7	1.6	1.1
Hexachlorobenzene	4	5.3	1.9	1.4
2,3,7,8-TCDD	8 ng	29 ng	23 ng	16 ng
Tetrachloroethylene	1.8	2.0	2.2	3.8

Either catalysis process would lead to the observed decrease in emission of aromatic molecules. Scheme 2 shows the benzene formation from PVC thermal degradation. Starnes¹⁶ noted mechanistic aspect of the thermal degradation of PVC and showed that ordinary monomer units are converted into internal allylic chloride defects by a mechanism that may include the abstraction of hydrogen by triplet cation diradicals derived from polyene intermediates. Cyclization reactions seem likely to contribute to the termination of polyene growth. Table 7 and 8 show a list of products emission from pyrolysis of PVC and PVC in the presence of copper, copper(II) chloride and cupric oxide in an atmosphere of nitrogen at 300 °C and 600 °C respectively. The results show that the concentration of aromatic and chlorinated aromatic hydrocarbons in an atmosphere of nitrogen is higher than those obtained in an atmosphere of air except for the level of 2,3,7,8 TCDD. The concentration of aromatic and chlorinated aromatic hydrocarbons increased with increasing temperature.



Scheme 2. Benzene formation.

Table 7. The amount (μg) of organic gases products from the combustion of pure PVC and mixture of PVC with copper, copper(II) chloride and cupric oxide at 300 °C under nitrogen.

Product	PVC	PVC +Cu	PVC + CuCl ₂	PVC + CuO
Benzene	480	445	44	40
Toluene	30	11	8.2	6
<i>o</i> -Xylene	-	-	-	-
Naphtalene	-	-	-	-
Chlorobenzene	3	3.3	0.01	0.007
Ethyl benzene	1.2	-	-	-
<i>p</i> -Dichlorobenzene	-	0.012	0.005	0.001
<i>o</i> -Dichlorobenzene	0.09	0.015	0.0008	0.0003
1,2,5- Trichlorobenzene	-	-	-	-
1,2,4- Trichlorobenzene	0.1	-	-	-
1,2,4,5- Tetrachlorobenzene	0.045	0.06	0.001	0.0008
Pentachlorobenzene	0.02	0.028	-	-
Hexachlorobenzene	0.04	0.1	-	-
2,3,7,8-TCDD	-	-	-	-
Tetrachloroethylene	1	0.95	0.97	1.5

Table 8. The amount (μg) of organic gases products from the combustion of pure PVC and PVC in the presence of copper, copper(II) chloride and cupric oxide at 600 °C under nitrogen.

Product	PVC	PVC +Cu	PVC + CuCl ₂	PVC + CuO
Benzene	670	530	101	52
Toluene	158	121	75	3
<i>o</i> -Xylene	1.17	1.05	0.40	0.22
Naphtalene	4.7	3.75	0.53	0.3
Chlorobenzene	1.65	1.6	1.134	0.79
Ethyl benzene	5.3	5	3.9	3.1
<i>p</i> -Dichlorobenzene	0.45	0.5	0.15	0.085
<i>o</i> -Dichlorobenzene	11	11.7	2.8	1.95
1,2,5- Trichlorobenzene	1.6	1.4	11.5	0.7
1,2,4- Trichlorobenzene	6.5	7.6	3.1	2.15
1,2,4,5- Tetrachlorobenzene	8.2	7.5	3.15	2.35
Pentachlorobenzene	5	6.1	1.95	1.2
Hexachlorobenzene	5.25	6.6	2.39	1.57
2,3,7,8-TCDD	-	-	-	5ng
Tetrachloroethylene	1.3	1.75	1.7	3.4

Conclusion

The purpose of this study was to determine the harmful emission from combustion and pyrolysis of pure PVC and PVC in the presence of copper and copper(II) chloride and cupric oxide. The beneficial effects of the presence of copper and copper compounds (especially cupric oxide) are: (1) an increase in the formation of short chain hydrocarbons, (2) a decrease in the amount of the major aromatic hydrocarbons products formed and (3) a decrease in the amounts of HCl formed except when PVC is in the presence of CuCl₂. A disadvantage of the presence of copper or copper compounds is an increase in the amount of dioxin formation.

A suggestion can conclude from this study that presence of copper or its compounds could be used to control some pollutants emission.

References

1. Hamer G, *Biotechnol Adv.*, 2003, **22**(1-2), 71-79.
2. Travis Wagner Paul, A new model for solid waste management: an analysis of the Nova Scotia MSW strategy, *J Cleaner Production*, 2008, **16**(4), 410-421.
3. Pichtel J, Waste management practices, municipal, Hazardous and industrial, Taylor and Francis, CRC, New York, 2005.
4. Yasuda K and M Takahashi, The emission of polycyclic aromatic hydrocarbons from municipal solid waste incinerator during the combustion cycle, Air and waste management Association, 1998, **48**(6), 441.
5. Reis M F, Sampaio C, Brantes A, Aniceto P, Melim M, Cardoso L, Gabriel C F, Simao J P and Miguel, *Int J Hyg Environ Health*, 2007, **210**, 439-446.
6. Lanoir D, Trouve G and Delfose L, *Waste Management*, 1997, **17**(8), 475.
7. Jay K and L Stieglitz, *Chemosphere*, 1995, **30**(7) 1249.
8. Wagner J C and Green A E S, *Chemosphere*, 1993, **26**(11), 2039-2054.
9. Bockhorn H, Hornung, A, Troer j and Kraus M, *J Anal Appl Pyrol.*, 1999, **49**(1-2), 97-106.
10. Kim S, *Waste Management*, 2001, **21**(7), 609-616.
11. Li S, Chi Y, Li W, Li R, Qiu K, Li X, Yan J, Ma J and Cen K, *Huan Jing Ke Xue.(China Environ Sci.)*, 2001, **22**(2), 95-100.
12. Jimenez A, Lopez J, Vilaplana H and Dussel J, *J Anal Appl Pyrol.*, 1997, **40-41**, 201.
13. Blazso M and Jakab E, *J Anal Appl Pyrol.*, 1999, **49**(1-2), 125-143.
14. Marongiu A, Faravelli T, Bozzano G, Dente M and Ranzi E, *J Anal Appl Pyrol.*, 2003, **70**(2), 519.
15. Karayidirim T, Yanik J, Yuksel M, Sagiham M, Vasile C and Bockhorn H, *J Anal Appl Pyrol.*, 2006, **75**(2), 112-119.
16. Starnes W H, *Progr Polymer Sci.*, 2002, **27**(10), 2133-2170.
17. Grimes S M, Lateef H, Jafari A J and Mehta L, *Polymer Degrad Stabil.*, 2006, **91**(12), 3274.
18. Ian C McNeil, L Memetea and W Cole. J, *Polymer Degrad Stabil.*, 1995, **49**, 181.



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