COMBUSTION OF PVC

Michael M. O'Mara

B.F.Goodrich Chemical Company, Technical Center, Avon Lake, Ohio 44012, USA

Abstract - The thermal decomposition and combustion mechanisms of PVC are examined.

With respect to thermal decomposition, the results of a deuterium labeling (d-PVC) study indicate that the mechanism of benzene formation involves an intramolecular cyclization step rather than an intermolecular Diels-Alder condensation step.

With respect to combustion, the evolution and ultimate fate of hydrogen chloride and other combustion gases generated under NBS Smoke Density Chamber conditions is described. The combustion of rigid PVC, flexible PVC and rigid PVC-wood mixtures has been carried out. It was observed that under smoldering conditions, rigid PVC evolves combustion gases in a sequence that agrees with the current mechanism of decomposition. It was discovered that under flaming conditions, the concentration of hydrogen chloride in the NBS Smoke Density Chamber rapidly decreases and that the decay follows first order kinetics. Analytical data is presented which shows that this decay is due to HCl condensation on the chamber walls and is not an experimental artifact. The data from these experiments indicate that water generated during combustion plays a key role in this conden-sation.

Recent data published on the exposure of test animals to the combustion gases from PVC are reviewed in light of the above findings.

INTRODUCTION

The combustion of polyvinyl chloride (PVC) has been the subject of considerable research over the past 20 to 30 years. The excellent ignition-resistant properties of rigid PVC and modified flexible PVC were responsible for many of its initial uses and for its continuing growth rate since the late 1930's to become the second most widely used plastic material in today's world market. The wide use and acceptance of PVC in applications demanding improved · fire performance is well documented (1). More recently however, combustion research relat-ing to PVC as well as other construction materials has been directed toward the by-products of combustion: heat, gases, aerosols, particulates and the effects of those by-products on biological systems. Indeed, one of the purposes of the present symposium is to delve into the complexity of just this issue, to determine what is known and what is not known and, hopefully, to outline what remains to be done. In this spirit then, this paper on the com-bustion of PVC will prove into the thermal decomposition of PVC (mechanisms), the combustion products from PVC, methods of altering the combustion profile of PVC and finally into the question of exposing test animals to the combustion products from PVC. Since the thrust of this paper will be directed toward the analytical chemistry of PVC combustion, it is relevant to ask what is the relationship between combustion toxicology or biological response and analytical chemistry. While some have suggested that the latter can predict the former (2, 3), recent published work on urethane foams, which produced a highly toxic bicyclo-phosphate ester during combustion, completely invalidates this approach when it is applied to broad classes of materials. In other words, a knowledge of the combustion gases released from a material does not allow one to predict, a priori, a biological response (4). However as was shown in this same report, ultimately it was analytical chemistry (specifically, phosphorous -31 nuclear magnetic resonance spectroscopy and chemical ionization mass spectro-metry) that unraveled the cause and effect observed in the biological testing. In essence, both disciplines are necessary and compliment each other in providing an improved under-standing of combustion toxicology.
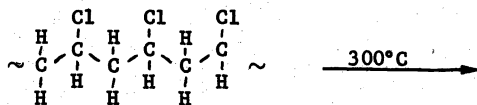
Thermal decomposition of PVC

HCl formation. The thermal decomposition of PVC has been the subject of extensive research over the years. Much of this has been directed toward thermal decomposition during process-ing and the role of stabilizers on this decomposition (5). This background of information provides insight into the very early steps of thermal decomposition. It is well recognized that the first step in the thermal decomposition of PVC is loss of hydrogen chloride. Kinetic and analytical data indicate that this initial dehydrochlorination occurs at "weak points"[*] along the PVC polymer chain. Once this initial dehydrochlorination takes place, an unzipping of hydrogen chloride occurs which accounts for the observations of color formation (polyene chains) and increased molecular weight (formation of tertiary carbons via inter-molecular bond formation).

It must be remembered that the above steps occur very early in the decomposition cycle and in fact are still the subject of considerable debate and research. It is more to the point to consider what happens under more severe thermal exposures than in those studies above which were generally in the temperature region of 150-200°C. In 1968, Boettner and co-workers published on the thermal decomposition of PVC by using thermal gravimetric analysis. In this work, PVC was heated from ambient to 600°C at 3°C per minute and polymer weight loss was re-corded. At approximately 275°C, a very rapid weight loss occurred accounting for approxi-mately 60% of the initial weight (Figure 1). A chemical analysis of the by-products of this
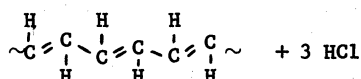
Figure I. WEIGHT LOSS vs. TEMPERATURE PROFILE for PVC RESIN [reference 6]
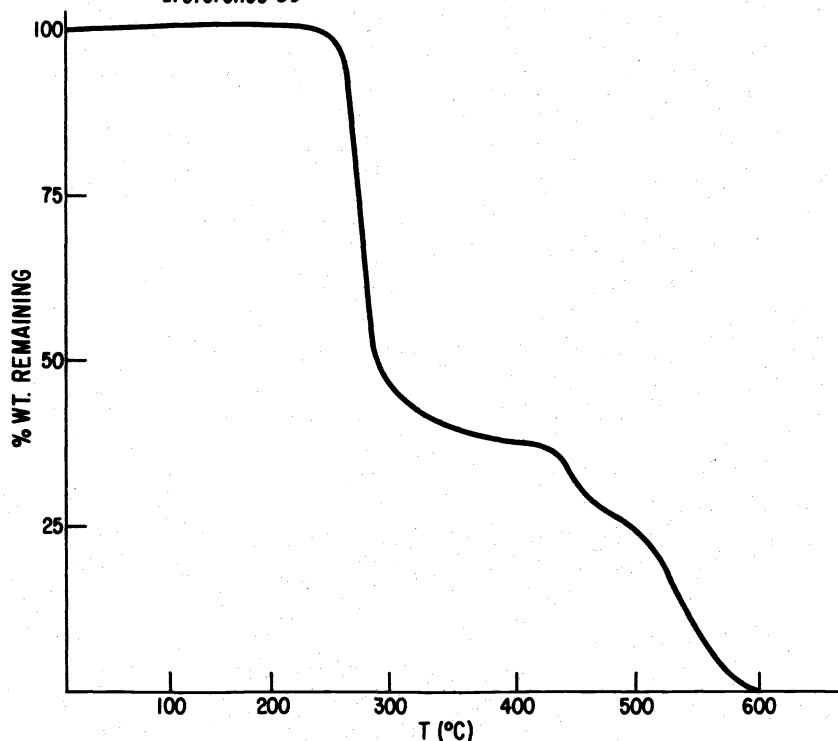
weight loss indicated a fraction consisting of 95% hydrogen chloride and 5% benzene. Thus, this analysis indicated the presence of the following mechanism:

$$\sim \underset{\underset{H}{\overset{H}{|}}}{C} \overset{\overset{Cl}{|}}{\underset{\underset{H}{\overset{H}{|}}}{C}} \overset{\overset{H}{|}}{\underset{\underset{H}{\overset{|}}}{C}} \overset{\overset{Cl}{|}}{\underset{\underset{H}{\overset{H}{|}}}{C}} \overset{\overset{H}{|}}{\underset{\underset{H}{\overset{|}}}{C}} \overset{\overset{Cl}{|}}{\underset{\underset{H}{\overset{H}{|}}}{C}} \sim \quad \xrightarrow{\quad 300°C \quad}$$

---

[*]Defined as allylic or tertiary carbon-chlorine bonds.

~C=C\C=C~C=C~   + 3 HCl

(a polyene)

At higher temperatures, it was found that the dehydrochlorinated polyene chain underwent scission with the subsequent formation of benzene and other aromatic (and aliphatic) hydrocarbons. The existence of benzene in the initial weight loss fraction suggests that this chain scission is occurring to a small extent at temperature around 300°C. The degree of this chain scissioning at lower temperatures was recently challenged by Michelson and co-workers (7). In their work which involved a TGA connected to a mass spectrometer, the results indicated that at 240°C under a helium purge, PVC degraded to hydrogen chloride and benzene simultaneously. This observation was accomplished by ion focusing at M/e = 78 (benzene) and M/e = 36 (HCl) continuously during the decomposition.

This is a startling observation since it suggests that both dehydrochlorination and chain scission occur simultaneously. Indeed, their data indicated that the mole ratio of hydrogen chloride to benzene was 2.5:1 during the initial weight loss (approximately 63% weight loss from ambient to 350°C).

Before this new proposed mechanism for PVC decomposition (simultaneous dehydrochlorination-carbon chain scission) can be accepted, the authors must account for the remaining chlorine in PVC. It can be shown that their study only accounts for 58% of the chlorine in PVC. It is possible that a significant quantity of the hydrogen chloride released in their system was adsorbed on surfaces prior to their analytical detector (mass spectrometer) (8). If this did happen, then no real conclusions can be drawn about the time sequencing of hydrogen chloride and benzene released from decomposing PVC. Nevertheless these authors have opened up an interesting avenue in the decomposition mechanism of PVC since the precise time sequence of dehydrochlorination and hydrocarbon formation has never been determined experimentally.

Mechanism of benzene formation. The formation of benzene during the thermal decomposition of PVC has always been assumed to take place by an intramolecular cyclization of the dehydrochlorinated polyene chain:

a vinyl or polyene radical

cyclization

1) C-C scission
2) aromatization

~ • +
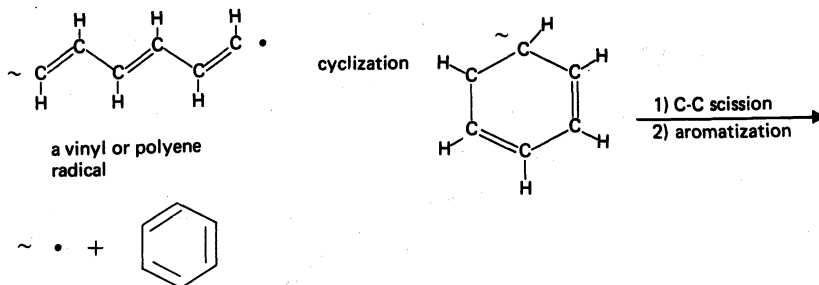
To account for the crosslinking that takes place early in the decomposition of PVC, Razuvaev* proposed a Diels-Alder type condensation between neighboring polyene chains (8):

(Diels-Alder Adduct)
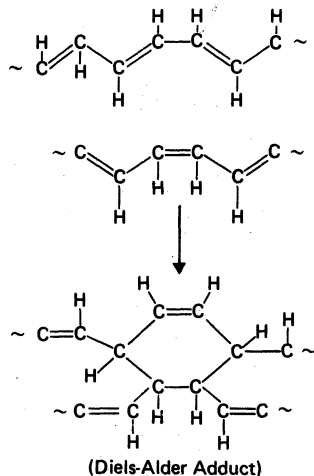
*This proposal has been (and continues to be) made by a number of investigators.

Such a mechanism accounts for the increase in molecular weight observed early in the decomposition of PVC. It also offers an alternative mechanism for benzene formation. The subsequent collapse of the above adduct would lead to benzene. To distinguish between an intramolecular cyclization reaction and a Diels-Alder intermolecular reaction is very important. If the latter is responsible for benzene formation, then it may be possible to alter this cyclization during decomposition with selected additives and thereby alter the evolution of organics during complete decomposition.

To distinguish between these two mechanisms, a deuterium labelling study was carried out. A mixture (50/50, mole) of poly (vinyl) chloride and poly (d_3-vinyl chloride) (10) was prepared by repetitive co-precipitation from THF with methanol. Scheme 1 provides a summary of what decomposition products might be expected from this intimate mixture depending upon which mechanism is in operation. Thus, if an intramolecular mechanism is in operation only h_6-benzene and d_6-benzene should be produced; if a Diels-Alder mechanism is in operation then a d_2h_4-benzene and a h_2d_4-benzene should be produced along with the h_6- and d_6-benzenes. In addition, the two hydrogen or deuterium atoms must be in a 1,2 position on the benzene ring.

Scheme 1:   Possible Decomposition Products (Benzenes) Resulting From
            PVC/d-PVC Mixture
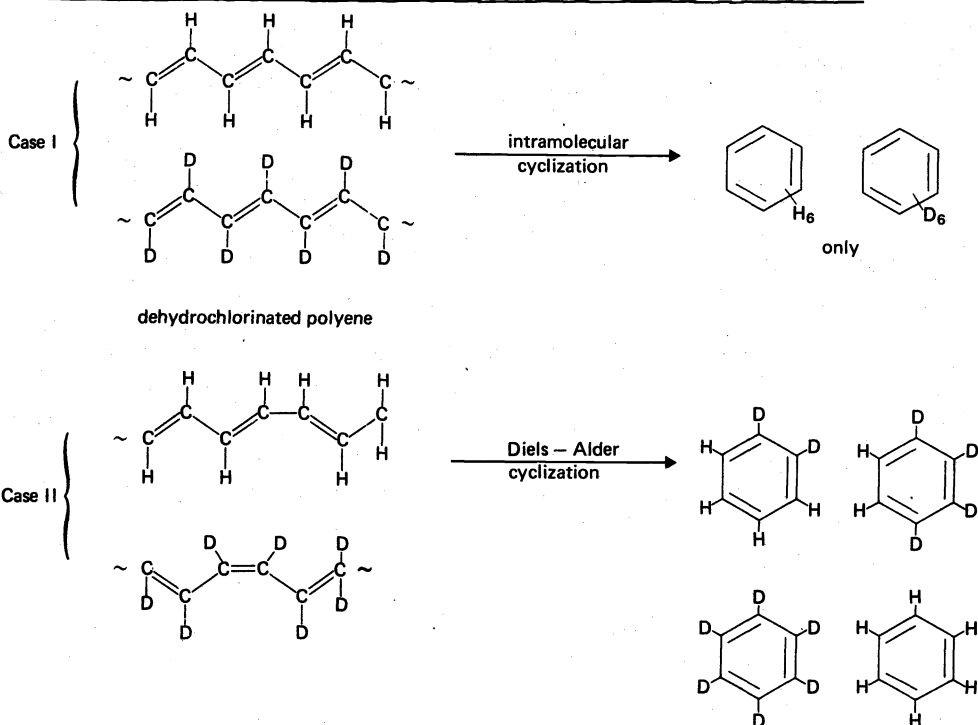
The PVC and d-PVC mixture was pyrolyzed at 580°C in a pyrolyzer-gas chromatograph-mass spectrometric tandem system designed for polymer decomposition studies (11).

> [In a typical run, 10 mg of the mixture was pyrolyzed at 580°C in a helium
> flow of 50 cc/minute. The pyrolysis products were swept onto a chromato-
> graphic column and separated. The entire benzene (all benzenes) peak was
> then directed into a CEC model 21-103C mass spectrometer through a molecular
> separator and the mass spectrum of the total mixture was recorded. In order
> to carry out a quantitative analysis, each of the ions from M/e = 78 to
> M/e = 84 was rendered monoisotopic by solving the appropriate 7 X 7 matrix.
> This in turn was accomplished by measuring the cracking patterns and
> sensitivities for pure C_6H_6 and C_6D_6 and calculating cracking patterns for
> $C_6H_5D_1$, $C_6H_4D_2$, $C_6H_3D_3$, $C_6H_2D_4$ and $C_6D_5H_1$ based on an average sensitivity
> of C_6H_6 and C_6D_6. There was only a 6% difference in sensitivities between
> C_6H_6 and C_6D_6.]

Before discussing the results of this experiment it should be noted that finding significant quantities of $C_6H_4D_2$ and $C_6D_4H_2$ in the pyrolyzate does not, by itself, prove the existence of the Diels-Alder type mechanism. Since the position of either the deuterium or hydrogen atoms on benzene cannot be determined by mass spectrometry due to hydrogen scrambling (12), another method (i.e., [1]H-N.M.R.) would be necessary to thoroughly characterize the benzenes. Fortunately this was not necessary to do because only two kinds of benzene, C_6H_6 and C_6D_6

were found in the pyrolyzate. The results of the computer solution of the ion species matrix
are summarized in Table 1.

TABLE 1. Distribution of Benzenes formed during the inert pyrolysis of a
          50/50 Mole mixture of PVC and d-PVC

Species	M/e	Mole, %
C_6H_6	78	46.8
$C_6H_5D_1$	79	2.1
$C_6H_4D_2$	80	0.4
$C_6H_3D_3$	81	0.4
$C_6H_2D_4$	82	0.7
$C_6H_1D_5$	83	4.6
C_6D_6	84	45.0

It is apparent from this analysis that only a mechanism involving intramolecular cyclization
to form benzene is valid. The data clearly show that a Diels-Alder type cyclization between
adjacent polymer chains cannot be invoked to explain the formation of benzene since only
traces of either $C_6H_4D_2$ or $C_6H_2D_4$ were found.

This work does not totally eliminate a Diels-Alder type reaction. Experiments like the
above but under different pyrolysis conditions (lower heating rates, presence of oxygen,
presence of thermal stabilizer) would be required before the mechanism could be completely
dismissed.

Combustion of PVC

Products of combustion. The combustion products from PVC have been well characterized.
Based on the above decomposition mechanisms, it is reasonable to assume that hydrogen
chloride, certain hydrocarbons, oxides of carbon and smoke are all produced during the com-
bustion of PVC. With respect to the gases, Boettner was one of the first analytical chemists
to completely characterize the combustion products from a wide series of PVC resins and com-
pounds (6). A typical list of the combustion products from PVC are summarized in Table 2.
It is obvious that the absolute quantity of these products will change depending upon the
specific conditions of combustion. The effect of combustion conditions on the combustion
gases released from PVC and other polymers has been described (13).

TABLE 2. Typical combustion products from PVC: Quantitative and
          Qualitative Analyses[6]

Component	mg/g
HCl	583
CO	442
CO_2	729
CH_4	4.6
C_2H_4	0.6
C_2H_6	2.2
C_2H_3Cl	0.6
C_4H_8	0.2
C_4H_{10}	0.3
C_5 hydrocarbons	0.3
C_6 hydrocarbons	0.3
benzene	36.0
toluene	1.3

Another combustion product from PVC that is often mentioned is phosgene. The most extensive
analytical study on the formation of phosgene from PVC was done by Woolley who carried out
well designed analytical seeding studies (phosgene seeded into analytical system to verify
detection capability). After redesigning his analytical hardware to circumvent experimental
artifacts, he showed that phosgene was not a combustion product from PVC at the 100 ppm
(weight phosgene/weight PVC) level (14).

Rate of combustion gas build-up. While a qualitative and quantitative analysis of the combustion products from any polymer is informative, this approach tells us nothing about the rate of build-up of combustion products in an enclosure or more importantly in a full-scale fire. For example in full-scale fires involving PVC and wood which were carried out by the National Bureau of Standards, it was reported that the release of hydrogen chloride from PVC was far below that which was theoretically expected (15).

In our studies on the combustion of PVC we have used the NBS Smoke Density Chamber and a variety of analytical techniques (nondispersive infrared, gas chromatography, chemiluminescence, specific ion electrodes and mass spectrometry) to follow the build-up of combustion products from PVC. In these experiments, milled and pressed sheets of PVC (Geon 103EPF7, 100 parts; polyethylene lubricant, 0.25 parts; metal ester stabilizer, 2.0 parts) were subjected to NBS Smoke Density Chamber testing (flaming and smoldering). Specifically smoke, hydrogen chloride, carbon monoxide and carbon dioxide were monitored. Experimental details are included in an Appendix at the end of this paper.

PVC and smoldering conditions. A plot of gas concentration/smoke verses time for the combustion of rigid PVC under NBS Smoke Density Chamber (smoldering, 2.5 watts/cm^2) conditions is presented in Figure 2. This profile indicates the relative evolution in time of the

Figure 2. COMBUSTION of PVC UNDER NBS SMOLDERING CONDITIONS
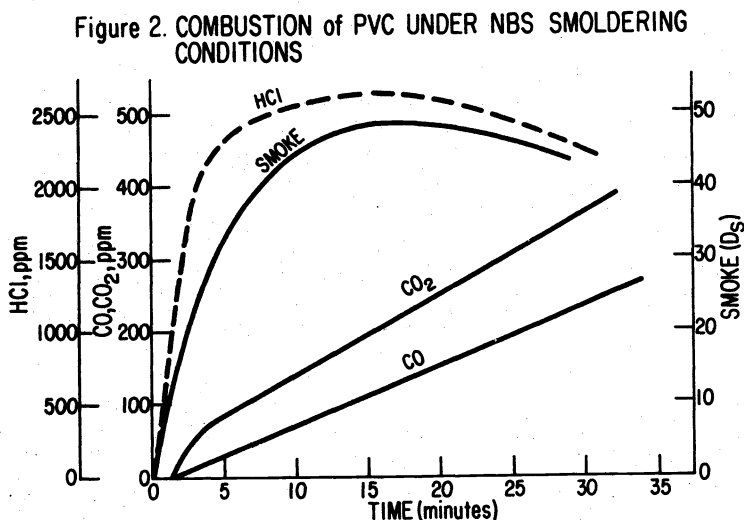
primary products of combustion from PVC under the experimental conditions. The data is also tabulated in Table 3. This profile is very consistent with the known decomposition mechanism

TABLE 3. Evolution of combustion products from PVC as a function of time under smoldering conditions[a]

time (minutes)	CO (ppm)	CO$_2$	time (minutes)	Smoke D$_S$	time (minutes)	HCl (ppm)
5	30	84	2	18	1	198
10	75	140	5	34	3	2026
15	110	195	7	40	5	2346
20	150	250	10	44	7	2431
25	190	305	13	48	9	2431
30	240	361	15	48	11	2515
34	270	-	18	49	13	2559
					15.5	2687
					19	2431
					25	2431

[a]NBS Smoke Density Chamber, 2.5 watts/cm^2; sample weight: 4.7g.

of PVC: rapid dehydrochlorination followed by smoke evolution. Once these products have been released from the polymer, the remaining char slowly oxidizes to carbon dioxide and carbon monoxide. It can be seen that linear rate of evolution of carbon monoxide and carbon dioxide develops. This is interpreted as resulting from the condensed phase oxidation of the carbon char remaining after the PVC has been dehydrochlorinated. In running additional experiments but with different masses of PVC, it was noted that the char tended to intumesce away from the sample holder toward the radiant heater. In general as the mass of the PVC sample was increased, the mass of the resulting char increased and that the distance between the char and the radiant heater decreased. Thus as the sample of PVC was increased, the amount of char resulting after the dehydrochlorination step was greater but also was subjected to a higher heat flux than 2.5 watts/cm^2. In light of this, it was expected that this change (increase) in heat intensity would increase the rate of carbon oxide formation. The distinction between yield and rate of formation should be made. Increasing the intensity of the source does not necessarily increase the yield of carbon oxide products but it should increase the rate at which those products are formed.

Experiments with various masses of PVC did show the presence of a mass-induced enhancement of carbon oxide release rate. These data are summarized in Table 4. It can be seen that there

TABLE 4. Effect of Sample Weight on the rate* (ppm/minute) of carbon oxide formation from PVC

Sample Weight, g	CO Rate	CO$_2$ Rate
	(ppm/minute)	
2.76	5.9	7.9
6.48	8.2	11.0
5.54	12.4	--
8.35	16.5	17.9
11.43	22.4	21.8

*Obtained from a linear regression of concentration verses time plots which were all linear.

is an approximate 3 - 4 fold increase in the rate of CO and CO$_2$ production as the amount of PVC is increased. This phenomenon points up one source of error in measuring combustion gases. If carbon monoxide monitoring from PVC becomes an important measurement in a combustion experiment, then it is obvious that the physical process of char formation cannot be ignored. If reproducible results are to be expected then the char must form in the same way (relative to the ignition source) each time.

Rigid PVC and flaming combustion. Testing PVC under flaming conditions is probably more representative of real fire conditions. In this mode of combustion, both radiant heat and a flame are used to ignite and burn the sample. A typical experiment involving the combustion of PVC under flaming conditions is shown in Figure 3; gas data are summarized in Table 5.

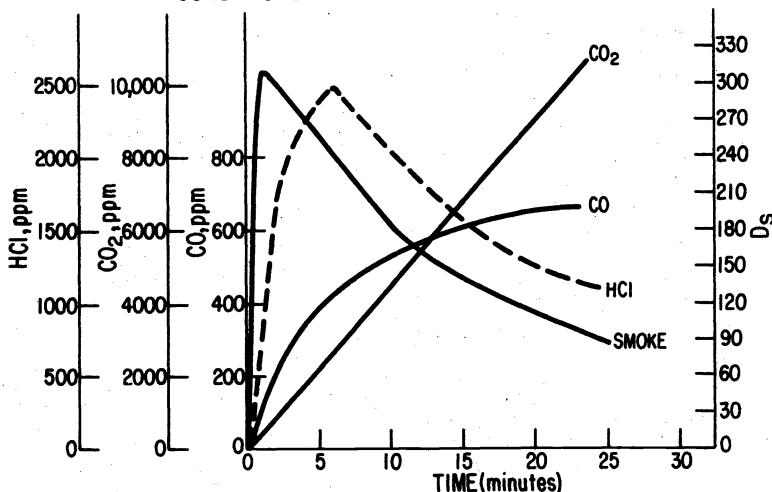Figure 3. COMBUSTION of PVC UNDER NBS FLAMING CONDITIONS

TABLE 5. Evolution of combustion products from PVC as a function of time under flaming conditions[a]

Carbon Oxides			Smoke		HCl	
Time (minutes)	CO	CO$_2$[b] (ppm)	Time (minutes)	D$_s$	Time (minutes)	ppm
1.0	50	420	0.5	54	.5	558
2.0	212	853	1.0	127	2.25	1870
5.0	375	2150	1.3	307	3.5	2148
10.0	525	4332	2.0	298	4.5	2350
15.0	580	6510	10.0	179	6.0	2476
20.0	675	8725	17.0	122	8.0	2274
			25.0	87	11.6	1946
					17.0	1491
					25.0	1018

[a] Sample weight: 4.66 grams

[b] These data were corrected for the CO$_2$ in the air but not for the CO$_2$ generated from the propane burner.

Consistent with previous smoldering data we see the separation in time between hydrogen chloride/smoke formation and carbon oxide formation. The presence of the flame obviously increases the rate of production of all gases. The presence of the flame induces a much more significant effect than just an increase in the rate of evolution of combustion gases. Comparing Figures 2 and 3, it can be seen that the presence of the flame (Figure 3) leads to a significant depletion of both hydrogen chloride and smoke as a function of time inside the NBS Smoke Density Chamber. This coagulation phenomenon was further explored in other PVC systems to see if it was specific only to rigid PVC.

Flexible PVC and flaming conditions. In these experiments, a flexible PVC wire formulation (31.8% chlorine) was burned in the NBS Chamber under flaming conditions. To verify that hydrogen chloride coagulation/condensation was taking place and that the above observation was not an artifact of the experiment, metal probes with a total surface area of 7.25 in^2 were placed in the chamber during the combustion experiment. The release and decay of hydrogen chloride was followed as a function of time and the metal probe was analyzed for chloride ion after the experiment. The ratio of probe surface area to wall surface area was determined and the theoretical amount of chloride that should have condensed on the wall surfaces inside the chamber was calculated. These calculations and data are summarized in Table 6 for two separate determinations. It can be seen that there is excellent agreement

TABLE 6. Condensation of HCl during the flaming combustion of flexible PVC[a]

	Run #1	Run #2
Weight of sample, g	2.0	14.0
Theoretical total chloride absorbed, g	0.6	4.5
Chloride found[b] on 7.25 in^2 probe, moles X10^{-5}	2.51	16.4 ± .4
Approximate surface temperature and area in NBS Smoke Density Chamber	27°C	6000 in^2
Chloride on 6000 in^2 surface, g	0.7	4.8

[a] Contains 31.8% chlorine.

[b] Determined by extracting probe with 10.00cc of distilled water and analyzing the solution with an Orion ion electrode.

between the theoretical amount of chloride that should have condensed on the walls of the chamber and the amount of chloride that did condense on the walls (based on probe analysis). It is obvious that under flaming conditions, hydrogen chloride is not stable in the atmosphere and will condense on colder surfaces. A plot of the combustion gases released from the flexible PVC compound verses time is shown in Figure 4. From a number of experiments

Figure 4. COMBUSTION of FLEXIBLE PVC UNDER FLAMING CONDITIONS
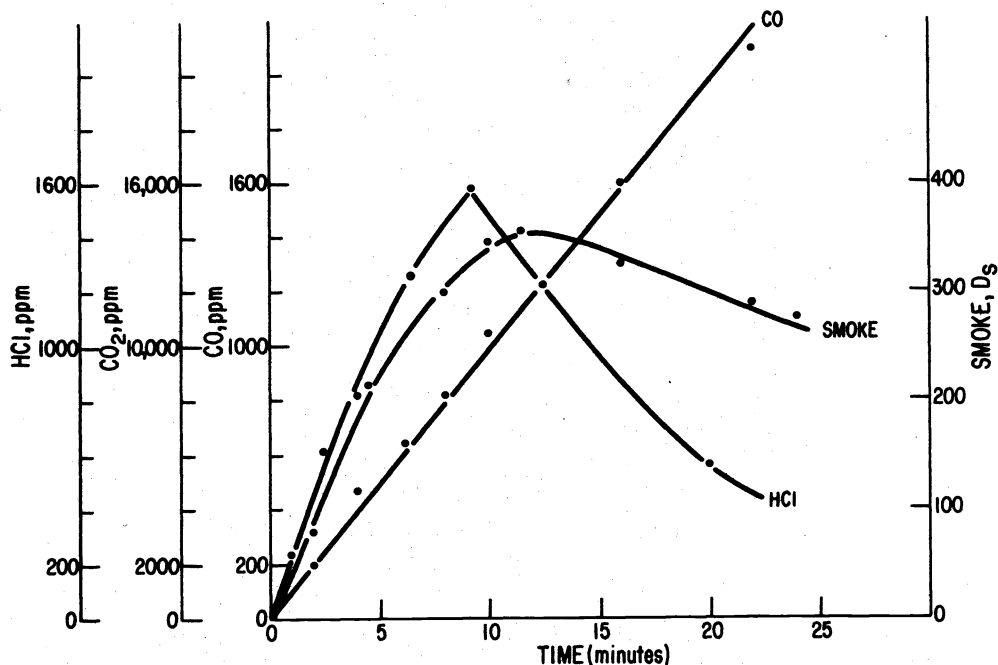
like this, first order decay rates of hydrogen chloride were determined. Typically these rate values averaged around k = 0.15 ± .05 min^{-1} or a half-life of approximately 8 minutes. It should be noted that there is considerable deviation in this rate of decay. Typically the rate constant can vary as much as ±50%. Nevertheless, these studies clearly show that in the presence of a flame, PVC does burn and decompose but the hydrogen chloride released is susceptible to rapid decay by condensation on nearby surfaces.

Combustion of PVC-wood mixtures. The combustion of PVC under smoldering conditions did not lead to a situation in which the atmospheric concentration of hydrogen chloride decreased rapidly after initial combustion (see Figure 2). In so far as flaming combustion induced this phenomenon, it strongly suggested that the presence of water is necessary for this depletion of hydrogen chloride to take place. It should be noted that the smoldering combustion of PVC is a relatively "dry" process. Initial pyrolysis leads to hydrogen chloride, organics and smoke formation with little evidence of true oxidation taking place. Oxidation comes later in the process when the carbon char, remaining after the pyrolysis step, is slowly oxidized. Since this char contains little hydrogen, water formation cannot occur during this condensed phase oxidation. Thus the amount of water formed during combustion is significantly lower under smoldering conditions than under flaming conditions. If the presence of water during combustion is necessary for hydrogen chloride depletion in the atmosphere, it is reasonable to expect this to occur when PVC is burned under smoldering conditions in the presence of a second material that will generate water of combustion. Since the destructive distillation (i.e., pyrolysis or smoldering combustion) of wood yields significant quantities of water, it is to be expected that the smoldering combustion of PVC-wood mixtures would provide the right conditions for rapid hydrogen chloride depletion in the atmosphere. To experimentally verify this, strips of white pine and PVC were placed side by side in the NBS Smoke Density Chamber sample holder. In this way, both materials could burn simultaneously. The results of this experiment are shown in Figure 5 and tabulated in Table 7. The first order rate decay of hydrogen chloride observed in this PVC-wood experiment is shown in Figure 6. Since hydrogen chloride is rapidly being depleted throughout the entire combustion experiment, it is obvious that a theoretical yield of hydrogen chloride will never be attained in the gas phase. For the present system, calculations for the percent HCl recovery, yield expected, etc. are presented in Table 8. It can be seen that for the 75%/25% wood-PVC mixture only 43% of the theoretical hydrogen chloride that should be in the atmosphere is actually there. This value is relative to a 76% recovery recorded for the same amount of PVC, burned under the same conditions except for the absence of wood (see Figure 2 and Table 8).

Combustion of PVC and Animal Toxicity. It is now believed that the ability of hydrogen chloride to condense from the atmosphere is responsible for the wide range of results reported on the toxicity of the combustion products from PVC. For example, in 1969 Cornish reported that a correlation between animal mortality and blood carboxyhemoglobin was observed in studies on

Figure 5. FATE of HYDROGEN CHLORIDE DURING the
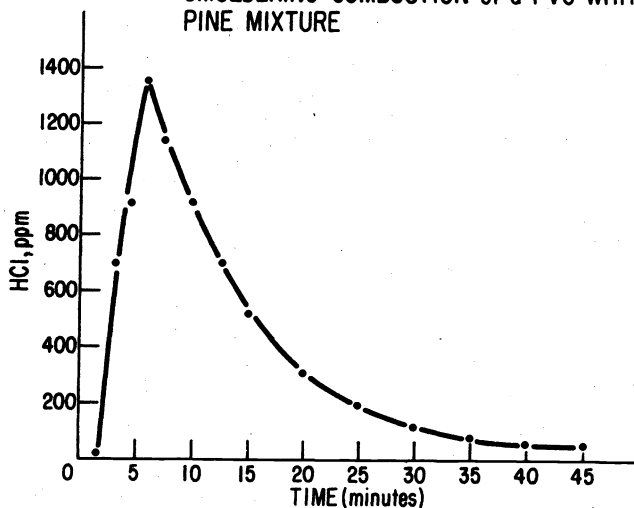SMOLDERING COMBUSTION of a PVC-WHITE
PINE MIXTURE

TABLE 7. Concentration of atmospheric hydrogen chloride during the smoldering
combustion of a PVC (25%) - white pine (75%) mixture

conditions: NBS Smoldering

sample weights: PVC: 4.12g; white pine: 10.65g

Time (minutes)	Hydrogen Chloride, ppm
1.5	23
3.0	704
4.5	919
6.0	1350
7.5	1144
10.0	919
12.5	645
15.0	464
20.0	311
25.0	196
30.0	121
35.0	86
40.0	63
45.0	55

the combustion of PVC (16). This result suggested that hydrogen chloride played a minor role
in animal intoxication. On the other hand, Kishitani showed in his studies that blood car-
boxyhemoglobin could not account solely for animal deaths during the combustion of PVC (17).
His results suggested that hydrogen chloride played a significant role in animal mortality.

Based on the analytical data presented in this paper on PVC combustion, it is suggested that
these two results on animal exposure to the combustion products from PVC are not in conflict
but rather point to the effect of experimental conditions on biological response. Animal
exposure times in Cornish's study were four hours and based on the half-life of hydrogen
chloride decay presented above, it might be expected that the actual exposure time to
hydrogen chloride in this experiment was much shorter. Kishitani's method involved five
minute exposure times so hydrogen chloride condensation from the atmosphere was probably
not a significant factor.

Clearly, hydrogen chloride, like any hydrogen halide released from a halogenated fire-
retarded material during combustion, is toxic. However the degree to which this acid gas

Figure 6. DEPLETION of HCl in ATMOSPHERE DURING
PVC-WHITE PINE SMOLDERING COMBUSTION

SLOPE : 0.092 ± .003
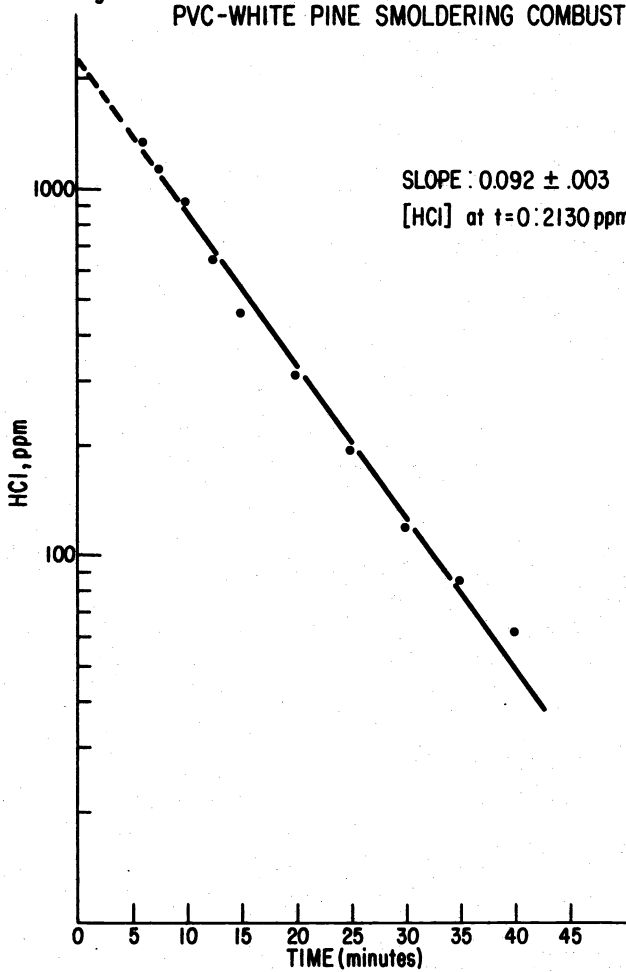[HCl] at t=0:2130 ppm

HCl, ppm

TIME (minutes)

TABLE 8. Theoretical and experimentally determined yield of hydrogen chloride
from PVC-white pine smoldering combustion

Amount of rigid PVC: 4.12g

Amount of white pine: 10.65g

NBS conditions: smoldering

Theoretical yield of hydrogen chloride: 3100 ppm

Experimental yield of hydrogen chloride if burned in the absence } 2350 ppm
of wood under smoldering conditions (from Table 4) (76%)

Experimental yield of hydrogen chloride when burned in the } 1350 ppm
presence of wood (43%)

contributes to animal mortality is completely dependent upon its concentration in the atmosphere and its subsequent transport to the biological detector. It is not surprising that varying experimental combustion-biological models will provide conflicting results.

The analytical data presented in this paper also shows that exposing PVC alone to radiant heat (no flame) provides a toxic atmosphere that is not representative of an atmosphere that would be created when that same polymer is burned under the same conditions but in the presence of another material.

This then answers the question about the role of analytical chemistry in combustion toxicology. Without it, no real unifying sense can be brought to the various exposure models now in existence nor can the ultimate question - what is the relevance of a particular small scale test to an actual fire - be answered. In the absence of good, hard, analytical data we have nothing more than an infinite number of experiments and an infinite variety of animal responses.

Experimental

Thermal Decomposition
Additional experimental details of the high temperature pyrolysis methodology used in the deuterium labelling study can be found in references 11 and 18.

Combustion
See references 19 and 20 for additional experimental information.

HCl analysis. The following technique was used to monitor hydrogen chloride in the NBS Smoke Chamber. A small circulating pump (12 liters/minute) was used to continuously withdraw a stream of the combustion gases from the geometric center of the chamber through a $\frac{1}{2}$ in Teflon® tube. The output of the pump was directed back into the chamber through a port at the top of the chamber. All transfer lines were Teflon®. An injection port was placed in the external Teflon® line so that an aliquot of the gas stream could be withdrawn. Disposable plastic syringes were used to withdraw samples of the gas periodically throughout the combustion experiment. Once the gas was obtained in the syringe, 2.00cc of an absorbing solution was drawn into the syringe and the syringe was vigorously shaken for 20 seconds to completely absorb the acid gas. The water was then transferred to a small beaker and analyzed with an Orion chloride ion electrode (Model 94-17 with Model 90-02 double junction reference electrode). The method was checked by seeding anhydrous hydrogen chloride gas into a dry glass vessel. The glass vessel was dried by flaming the vessel under a dry nitrogen flow. Recovery of hydrogen chloride from this system by the syringe method described above was 102 ± 2% over a concentration range of 100 - 1000 ppm.

REFERENCES

1. M. M. O'Mara, W. Ward, D. P. Knechtges, R. J. Meyer, "Fire Retardation of Polyvinyl Chloride and Related Polymers", Flame Retardancy of Polymeric Materials, ed. Marcel Dekker, Inc. 1973, p. 195-272 and references therein.

2. K. Sumi, Y. Tsuchiya, J. Fire and Flammability, 3, 46 (1972).

3. ibid, 4, 15 (1973).

4. I. Einhorn, Science, 187, 743 (28 February 1975).

5. See for example, the monograph Stabilization of Polymers and Stabilizer Processes, Advances in Chemistry Series #85, American Chemical Society, 1968, p. 1 - 81, and references therein.

6. E. A. Boettner and B. Weiss, J. Appl. Polym. Sci., 13, 337 (1969).

7. R. W. Mickelson, K. J. Voarhees and P. W. Ryan, "Correlation Between Thermal Analysis and Effluent Gas Analysis", Polymer Conference Series, University of Utah, July 7-11, 1975.

8. idib, page 14.

9. G. A. Razuvaev, Dokl. Adad. Nauk. SSSR 170 (6), 1342 (1966).

10. The sample of poly (d_3-vinyl) chloride was obtained from Dr. V. Folt, B.F.Goodrich Research Center, Brecksville, Ohio; H_1-N.M.R. indicated that the sample was 99.5% deuterated.

11. M. M. O'Mara, J. Polym. Sci., A-1, 8, 1887-1899 (1970).

12. K. R. Jennings, Z. Naturforsch, 22a, 454 (1967).

13. E. A. Boettner, G. L. Ball, B. Weiss, "Combustion Products From the Incineration of Plastics", U. S. Environmental Protection Agency Research Grant EC-00386, February 1973.

14. W. D. Woolley, Br. Polym. J., 1971, 3, 186. For additional studies on PVC fires by Woolley see: Plastics & Polymers, December 1973, 280.

15. I. N. Benjamin, National Bureau of Standards, private communication.

16. H. H. Cornish, E. L. Abar, Arch. of Environ. Health, 19, 15 (1969).

17. K. Kishitani, J. Faculty of Engineering, University of Tokyo (B), Vol. XXXI, No. 1, 1 (1971).

18. M. M. O'Mara, J. Polym. Sci., 9, 1387 (1971).

19. M. M. O'Mara, J. Fire & Flamm., 5, 34, January 1974.

20. M. M. O'Mara, Combustion Toxicology, 1, August 1974.