#### CHEMISTRY

#### V.P. Gupta

THE THERMAL DEGRADATION OF POLY (VINYL CHLORIDE)

#### ABSTRACT

This thesis describes an investigation of the thermal degradation of polyvinyl chloride. A technique involving the simultaneous measurement of HCl evolution and spin generation was used to study this decomposition reaction.

Four polyvinyl chloride samples containing different structural irregularities were employed. On the basis of measured activation energies for radical and HCl generation in these samples of controlled structure, an overall mechanism of degradation is proposed. The mechanism is a chain reaction involving a beta chloro elimination from a radical-containing polymer molecule. Molecules containing tertiary C-Cl bonds are chosen to undergo a fast initiation.

Those containing tertiary C-H bonds are also demonstrated to be highly unstable, but the instability is not associated with the initiation step.

The effects of oxygen and preirradiation by U.V. rays were studied using this technique. A mechanism

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## THERMAL DEGRADATION OF POLY (VINYL CHLORIDE)

by

Ved P. Gupta, Ph.D. (Lucknow)

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy

Department of Chemistry, McGill University, Montreal, Canada.

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September, 1970

To my parents

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Miss Margaret Stredder for her careful typing; and

colleagues and friends, who have been helpful, in many ways.

#### FOREWORD

An investigation into the thermal degradation of polyvinyl chloride is presented in seven chapters.

CHAPTER I: General Introduction

A brief survey of the problem and reasons for undertaking this investigation.

CHAPTER II:

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Preparation and characterization of experimental samples.

CHAPTER III:

Experimental techniques.

CHAPTER IV:

Mechanism of the thermal degradation of polyvinyl chloride.

CHAPTER V:

The effect of oxygen and ultra-violet irradiation on the thermal degradation of polyvinyl chloride. CHAPTER VI:

The effect of stabilizers on the degradation of polyvinyl chloride.

CHAPTER VII:

Contribution to original knowledge and suggestions for further work.

Four Appendices are included. They contain data for the number average molecular weight determinations; the derivation of the kinetic solutions of Chapter IV; Figures referred to in Chapter IV and VI, and supporting data for the figures in Chapters IV, V and VI.

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The effects of oxygen and preirradiation by U.V. rays were studied using this technique. A mechanism for the chain scission in the presence of oxygen is proposed and the effect of U.V. irradiation is rationalized.

The stabilizing action of organotin compounds was shown to be associated with active radical coupling and addition.

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# CHAPTER I

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### GENERAL INTRODUCTION

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#### I. INTRODUCTION

The investigation of the degradation of polymers has been a major area of research for almost three decades. With the production of new polymeric materials and increasing requirements of stability against different degradative agents, this deep interest continues.

In polymer chemistry, the term degradation was at one time defined as a "chemical process which causes a decrease in the molecular weight of the parent compound". Since this loss in the molecular weight of a polymer is usually accompanied by a considerable change in its physical and chemical properties, the definition of degradation has been replaced by "the deterioration of properties of polymers". The degradative agencies can be oxidation, high energy radiation (U.V.  $-\gamma$ -rays), heat, mechanical work, etc.

From the practical point of view, the degradation induced by heat is of prime importance, since, during fabrication, materials are subjected to high temperatures. For this reason, in the present work thermal degradation will be discussed at greatest length.

#### I-1. THERMAL DEGRADATION

It is well known that the chemical structure of a repeating unit is of primary importance in determining the thermal stability of polymers. Madorsky, Straus, Brown, Wall & Simha<sup>(1-4)</sup>, studied the effect of structure on the stability of polymers. They expressed their stabilities in terms of  $T_h$ , which is the temperature corresponding to 50% loss of weight of a given polymer sample in 40-45 minutes of heating under vacuo. Typical data are shown in Table I-1.

The data in Table I-l reveal a number of patterns.

1) The replacement of one or two hydrogen atoms on the backbone by alkyl groups such as  $CH_3$ results in a decrease in stability. Comparison of the stabilities of polypropylene with polyethylene, polymethylmethacrylate with polymethylacrylate; and poly- $\alpha$ -methylstyrene with polystyrene in the above Table support this observation.

2) The presence of double bonds in a  $\beta$ position to a substituent introduces a marked instability. Polybutadiene which includes a double bond has the same stability as that of polyethylene, while polyisoprene which has a C-CH<sub>2</sub> bond at a  $\beta$ 

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### TABLE I-1

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RELATIVE THERMAL STABILITIES OF ORGANIC POLYMERS <sup>(5)</sup>

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# (Based on temperature of half life, $T_{h}$ )

Polymer	Structure	T <sub>h</sub> *
		°c
Polyethylene	$\begin{bmatrix} -CH_2 - CH_2 \end{bmatrix}$ n	406
	CH3	
Polypropylene		387
Poly(ethylene oxide)		345
Polybenzyl		430
Poly-p-xylene	$\begin{bmatrix} -CH_{2} & -CH_{2} \\ H & H \end{bmatrix} n$	432
Polybutadiene	$\begin{bmatrix} -CH_2 - CH_2 - CH_2 \\ -CH_2 - CH_2 \end{bmatrix}_n$	407
Polyisoprene	$\begin{bmatrix} -CH_2 - CH = C - CH_2 \end{bmatrix}_n$	323
Polymethylacrylate	$\begin{bmatrix} -CH_2 - CH_{-} \\ COOCH_2 \end{bmatrix} n$	328
Polymethylmethacrylate	$\begin{bmatrix} CH_3 \\ -CH_2 - C - \\ C - \\$	283
Polystyrene	$\begin{bmatrix} -CH_2 \\ -CH_3 \end{bmatrix}$	364
Poly-a-methylstyrene	$\begin{bmatrix} -CH_{2} \\ -C$	287

T<sub>h</sub> is the temperature corresponding to 50% loss of wt. <sup>h</sup> of a given polymer sample in 40-45 minutes of heating under vacuo.

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position to the double bond is much less stable than is polypropylene.

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3) The inclusion of oxygen in the backbone reduces stability, whereas benzene rings increase the stability of polymers. The stability comparisons of poly(ethylene oxide) and polybenzyl with polyethylene clearly demonstrate this behaviour.

Studies on model compounds of polymers have demonstrated the fact that polymers are usually less stable than such models. For example, polyethylene could be expected to have a similar stability to a short chain paraffin such as hexadecane. However, it decomposes at a temperature~200°C. lower than does hexadecane. Similarly, from model compound studies, polyethylmethacrylate would be expected to yield olefins and acids as decomposition products, as do most simple carboxylate esters. However, on heating, a completely different set of products is derived, practically all of which are monomer units. The primary decomposition reaction is thus a sort of unzipping and is completely unrelated to the behaviour of the model compound.

There are at least two main rationales to explain this "size anomaly" of polymers. First, structural abnormalities exist in the polymer molecules at which degradative reactions are readily initiated and secondly,

- 4 -

many reactions of the model compounds which occur in a step by step manner, are converted to chain processes in the polymer molecule.

The most common reactive abnormalities present in the polymer molecules are associated with the double bonds which are "built in" during polymerization. For example, termination by disproportionation and/or chain transfer to monomer can generate double bonds in polymers.

Disproportionation

$$\sim CH_2 \stackrel{CH_3}{\underset{l}{\sim}} \stackrel{CH_3}{\underset{l}{\sim} } \stackrel{CH_3}{\underset{l}{\sim}} \stackrel{CH_3}{\underset{l}{\sim} } \stackrel{CH_3}{\underset{l}{\sim}} \stackrel{CH_3}{\underset{l}{\sim}} \stackrel{CH_3}{\underset{l}{\sim}} \stackrel{CH_3}{\underset{l}$$

and/or

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Transfer to monomer  

$$\sim CH_2$$
-CHCl + CH\_2=CHCl  $\longrightarrow \sim CH_2$ -CH\_2Cl + CH\_2=CCl (I-2)  
 $CH_2$ =CCl + CH\_2=CHCl  $\longrightarrow CH_2$ =CCl (-CH\_2-CHCl)  $\sim (I-3)$   
n
(I-3)

Other abnormalities which lower stability are chain branches or catalyst fragments which have been incorporated into the polymer chain. Depending upon the type of catalyst used, polymer chains may contain groups of the following kinds in terminal positions.

RCOO-CH<sub>2</sub><sup>~~</sup> group obtained from aryl or alkyl peroxide catalyzed reactions.

 $HSO_4$ -CH<sub>2</sub> group obtained from persulphate catalyzed reaction.

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On heating, these groups can decompose to initiate degradation reactions.

Processes involved with the thermal degradation of polymers can be grouped as follows : -

1) Depolymerization :

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In this group, the main product of thermal degradation are the monomers.

2) Ester Decompositions :

This describes the polymers which decompose into acids and olefins in the same manner as do short chain esters.

3) Random Chain Cleavage :

This class contains the polymers which yield short chain hydrocarbons and other chain fragments.

The first two groups are the classifications in which most polymers can be included. We will therefore discuss these in detail.

I-1-1. Depolymerization

Depolymerization describes the degradation path in which the degradation products are mainly monomers. Table I-2 shows the different yields of monomers from a number of organic polymers pyrolyzed in vacuum.

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## (6) <u>TABLE I-2</u>

#### YIELD OF MONOMER IN THE PYROLYSIS OF SOME ORGANIC POLYMERS IN VACUUM (IN PERCENT OF TOTAL VOLATILIZED)

Polymer	Temperature Range <sup>O</sup> C	Yield of Monomer, %			
Polyethylene	393-444	0.03			
Polypropylene	328-410	0.17			
Poly(ethylene oxide)	324-363	3.9			
Polymethylacrylate	292-399	0.7			
Polymethylmethacrylate	246-354	91.4			
Polytetrafluoroethylene	504-517	96.6			
Polystyrene	366-375	40.6			
Poly-m-methylstyrene	309-399	44.4			
Poly-a-methylstyrene	259-349	100			

In the above Table, the monomer yield is shown to vary from .03% to 100%. From this data, it is evident that any substitution for a hydrogen in the monomer unit results in monomer formation on pyrolysis of the polymer. The comparison of monomer yield for polyethylene with other polymers, in the above Table, demonstrates this pattern. Furthermore, a twofold substitution for hydrogen atom at a 1,1, position further increases the monomer

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- Construction and the second contract of the second second strategy space. All the second s second se second s second s second se yield. Comparison of polystyrene, with poly-m-methylstyrene, and poly- $\alpha$ -methylstyrene, and polymethylacrylate with polymethylmethacrylate, makes this evident.

Monomer formation, basically, is a result of rupture of a chain to form radicals. This rupture may commence at a chain end, at an irregularity in a chain, or randomly along the length of the chain. In polymers where the formation of radicals is not favoured, degradation products other than monomer are usually obtained.

#### I-1-2. Ester Decomposition

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A number of polymers, on heating, decompose into acids and olefins in the same manner as do short chain esters. Polymers such as polyvinyl acetate liberate acid and an unsaturated product is left behind as a residue.



Polyvinyl chloride, the polymer which is the subject of the current investigation, while not an ester in the ordinary sense, has been included in this class due to the similarity of its decomposition reactions.

## I-2. DEGRADATION OF POLYVINYL CHLORIDE

Polyvinyl chloride has been one of the world's most important commercial polymers for more than 40 years and as a consequence, it has been a subject of a vast amount of research aimed at the complete spectrum of synthesis, structure and property problems. Among these, a prime area of investigation has been that of thermal stability. It has a glass transition temperature of  $81^{\circ}$ C. <sup>(7)</sup> and consequently, during processing, and often in use, is subjected to elevated temperatures which cause it to undergo a chemical degradation. The degradation reaction is a complex one, which has been extensively studied <sup>(8-19)</sup>, but can generally be described as dehydrochlorination. This dehydrochlorination is accompanied by the formation of a series of conjugated double bonds. The overall process is pictured as follows:



The conjugated olefin sequences absorb in the visible light region and consequently, the degraded material can be highly coloured. The mechanism of the decomposition reaction has been investigated in detail by

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a number of authors (8 - 19), and three types of mechanisms, unimolecular, ionic and radical chain have been proposed.

I-2-1. The Unimolecular Mechanism

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The reactions involved in the dehydrochlorination of PVC were first described by Marvel & Horning<sup>(20)</sup>. In their view, the process was the following:

The loss of the first molecule of HCl creates a double bond which activates an adjacent chlorine atom by the "allylic effect" and an evolution of another mole of HCl takes place. This mechanism, shown below, has been supported by several other workers <sup>(9,13,19,21)</sup>.

$$PVC \longrightarrow -CH_{2}-CH=CH=CH-CHCl-CH_{2}^{-+} HCl \qquad (I-6)$$
$$-CH_{2}-CH=CH=CH-CHCl-CH_{2} \longrightarrow -CH_{2}-CH=CH=CH=CH=+ HCl \qquad (I-7)$$

Druesdow & Gibbs<sup>(9)</sup> propose a slightly modified unimolecular mechanism in which the reaction is initiated at some structural irregularity such as a double bond. In support of this contention is the work of Baum<sup>(13)</sup> who found that 4-chlorohexene-2 liberates HCl at a rate comparable to that of PVC.

1-2-2. The Ionic Mechanism

Small alkyl chloride molecules in the presence of base undergo reactions involving elimination, substitution or both<sup>(22)</sup>. In the case of PVC similar reactions can take place.

Elimination :

$$\begin{array}{c} c_{1} \\ -CH-CH- \longrightarrow -CH=CH- + BH^{+} + C1^{-} \\ B: \longrightarrow H \end{array}$$
(I-8)

Substitution :

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$$\begin{array}{c} \text{Cl} \\ -\text{CH}_2 - \text{CH}_- \longrightarrow -\text{CH}_2 - \text{CH}_- + \text{Cl}^- \\ \uparrow B_1 & B^+ \end{array}$$
 (I-9)

where B: is a base, strong or weak.

If the substitution is infrequent, then base degraded PVC gives a highly coloured product<sup>(23-25)</sup> similar in nature, to the long polyene chain found in thermal dehydrochlorination of PVC. Sodium methoxide and sodium in liquid ammonia both produce highly coloured products at room temperature.

I-2-3. The Radical Mechanism

The radical mechanism has found support from a large number of workers. Arlman<sup>(10,11)</sup> in 1954 proposed the following radical chain mechanism for the decomposition of PVC.

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In this mechanism, it is proposed that the reactions are initiated by the cleavage of an end group. Following this a mole of HCl is liberated from the monomer unit adjacent to a free radical. This "molecular" mechanism was based on the fact that the free radical initiators were observed to accelerate the rate of HCl evolution. The inability of free radical scavengers to reduce the rate of dehydrochlorination of polyvinyl chloride was explained to be due to a very stable freeradical intermediate.

In 1965, Ouchi<sup>(26)</sup> confirmed the presence of free radicals in the heat treated PVC by means of E.S.R. measurements and lent further support to the radical mechanism. Bengough<sup>(19)</sup>, however, rejected the chain mechanism on the grounds that he found the normal initiators to have no effect on the rates of dehydrochlorination. According to him, the dehydrochlorination is a

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free radical reaction, of the type shown below, but is not a chain process.

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$$chcl=ch-chcl-ch_{2}-chcl-ch_{2}-\rightarrow chcl=ch-ch-ch_{2}-chcl-ch_{2}-+cl \cdot (I-14)$$

$$cl \cdot + chcl=ch-ch-ch_{2}-chcl-ch_{2}-\rightarrow chcl=ch-ch=ch-chcl-ch_{2}-+hcl \cdot (I-15)$$

This is, in effect, an allylic activation process of the type proposed by the first workers in the field. (20)

Winkler<sup>(14)</sup> also postulated a free radical chain mechanism but in his case, the process was based on the early work of Barton and Howlett<sup>(27)</sup> and Fuchs & Louis<sup>(28)</sup>.

Fuchs and Louis<sup>(28)</sup> showed that on the chlorination of PVC, methylenic groups disappear and the major portion of the resulting product does not have 1,1 dichloro units, such as are present in the polyvinylidene chloride structure. This indicates that the major portion of a free radical attack is on the methylenic hydrogen atoms. Barton and Howlett<sup>(27)</sup>, showed that the decomposition of certain alkyl chlorides occur by a free radical <u>chain</u> process. The mechanism for the decomposition of 1,2,dichloroethane proposed by them is the following:

$$H - \stackrel{i}{C} - \stackrel{i}{C} - H \underset{H}{\longrightarrow} H - \stackrel{i}{C} = CH_2 + CI \cdot (I-17)$$

In this scheme the Cl· radical abstracts, a hydrogen atom from one carbon atom and 1,2,dichloroethyl radical is formed. This then loses another Cl· atom to continue the chain. By considering the structure of radical intermediates Barton predicted the mechanism for the decomposition of a number of alkyl chlorides and, in almost every case, his predictions have found experimental verification.

By combining the results of Louis & Fuchs and Barton & Howlett, the abstraction of methylenic hydrogen atoms by Cl· and the subsequent Cl· expulsion by the intermediate radical, a number of radical mechanisms have been outlined. Winkler's <sup>(14)</sup> is one of these. In his proposal the initiating radicals are postulated to come from catalyst residues left from the polymerization process or they could arise as the result of oxidation. The propagation step which follows is the abstraction of a methylene hydrogen atom.

 $( \cdot )$ 

$$R \cdot + -CHCl - CH_{2} - CHCl - CH_{2} - \longrightarrow RH + -CHCl - CHCl - CH_{2} - CHCl - CH_{2} - (I-18)$$

$$-CHCl - CH - CHCl - CH_{2} - CHCl - CH_{2} - \underbrace{\longrightarrow}_{2} Cl \cdot + -CHCl - CH - CH_{2} - CHCl - CH_{2} - (I-19)$$

$$Cl \cdot + -CHCl - CH - CH_{2} - CHCl - CH_{2} \rightarrow HCl + -CHCl - CH - CHCl - CH_{2} - (I-20)$$

At this same time, Stromberg, Straus & Achhammer<sup>(15)</sup>, proposed a similar radical chain mechanism but, according to them, the initiation step involved a Clatom which derived from the thermal cleavage of a C-Cl bond. The Cl· then goes through the sequence of hydrogen abstraction shown above.

Recently, Bamford & Fenton<sup>(29)</sup> have given further support to the free radical mechanism by the degradation of PVC in the presence of labelled toluene  $(C_6H_5CH_2T \& C_6H_5^{14}CH_3)$ . They found a linear relationship between the extent of T incorporation in the polymer chain and the extent of dehydrochlorination. They concluded that the degradation of PVC involves free radical intermediates. Such a mechanism was further supported in the same paper by a grafting experiment. PVC was degraded at  $120^{\circ}C$  in methylmethacrylate in the presence of triphenyl phosphine. After the degradation a graft copolymer of PVC and methylmethacrylate was obtained which, the authors concluded, showed that the degradation proceeds via a radical process.

From the foregoing discussion, it is evident that nearly every imaginable type of mechanism has been considered and proposed as being of importance in the degradation of PVC. However, the continuing debate over the mechanism makes it quite clear that there is insufficient evidence to select from among these, even though one of them may be correct. Thus, despite the continuing debate of more than three decades, it is clear that the mechanism of PVC degradation is still not satisfactorily understood. This state of affairs is not surprising when one considers that despite all of the published data, there exists only one set of energetics specifically associated with the overall HCl expulsion.

Since so many of the proposed mechanisms have involved a radical process, it would obviously be useful to begin the measurements of the rates and energetics associated with the presence of radicals. Such a measurement is possible at this time, by means of an electron spin resonance technique. In the present work, this technique has been used along with others in the investigation of the thermal degradation of PVC.

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#### 1-3. PRESENT INVESTIGATION

The objective of the present work is to determine the energetics of the various steps in the thermal degradation of polyvinyl chloride. Using these energies, and other data, a rationalization for an overall mechanism can be constructed.

In the degradation of PVC the question has arisen as to how reaction chains are initiated. By comparison to the thermal stability of 1,3,5 trichlorohexane, which is a model compound of PVC, it has been shown that the initiations of the chains can be associated with the presence of some "structural defects" in the polymer (30,31). These "defects" have been variously identified as end groups (9,19,32,33), branches (9,19,34), olefins (13,15,35), oxygenated segments (36), etc. The difficulties of positively identifying and quantitatively measuring small numbers of such groups in a macromolecule are obvious. Consequently, a certain amount of recent work has been directed towards the identification of the primary degradation steps by the utilization of model compounds of PVC<sup>(37)</sup>. In the present work, PVC samples containing tertiary hydrogen and tertiary chlorine were prepared and their degradations were studied by the E.S.R. - HCl technique.

The order of presentation is as follows:

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Chapter II describes the preparation and characterization of experimental samples of various structures.

In Chapter III, we have described the experimental techniques which have been used throughout this work. The experimental details of thermogravimetry and simultaneous measurements of HCl evolution and spin generation are discussed.

Chapter IV reports the experimental results of the degradation of four samples of different structures. The effect of the chain transfer agent, triphenylmethane, is also discussed. On the basis of the results, a (thermal) degradation mechanism of PVC in an  $N_2$  atmosphere is proposed, and the effect of structural irregularities is rationalized.

Chapter V describes the effect of O<sub>2</sub> and U.V. pre-irradiation on the thermal degradation of PVC, and a reaction mechanism for the degradation of PVC in the presence of oxygen is discussed.

In the last Chapter, Chapter VI, the effect of organotin stabilizers on the degradation of PVC is reported and a stabilization mechanism is postulated.

An Appendix is also included. This contains the Tables of original data for figures presented in this work. Also included, are the mathematical derivat-

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ions for the kinetic equations in Chapter IV and the osmotic pressure measurements of Chapter II.

I-4. REFERENCES

#### CHAPTER I

- L.A. Wall, S.L. Madorsky, W.D. Brown, S. Straus & R. Simha, J. Amer. Chem. Soc., <u>76</u>, 3430 (1954).
- S. Straus & S.L. Madorsky, J. Res. Nat. Bur. Stand., 50, 165 (1953) RP. 2405.
- S.L. Madorsky & S. Straus, J. Res. Nat. Bur. Stand., 53, 361 (1954).
- 4. S.L. Madorsky & S. Straus, J. Res. Nat. Bur. Stand., 55, 223 (1955).
- 5. S.L. Madorsky, "Thermal Degradation of Organic Polymers", Interscience Publishers 1964, p.295.
- 6. S.L. Madorsky, "Thermal Degradation of Organic Polymers", Interscience Publishers 1964, p.301.
- 7. F.D. Reding, E.R. Walter, and F. J. Welch, J. Polymer Sci., 56, 225 (1962).
- A.S. Kenyon, Symposium on Polymer Degradation Mechanism, Nat. Bur. Stand., Circular 525, p. 81 (1953)
- 9. D. Druesdow and C.F. Gibbs, Ibid. 525, p. 69 (1953).
- 10. E.J. Arlman, J. Polymer Sci., 12, 547 (1954)
- 11. E. J. Arlman, J. Polymer Sci., 12, 543 (1954).
- 12. L. H. Wartman, Ind. Eng. Chem., 47, 1013 (1955).
- 13. B. Baum & L.H. Wartman, J. Polymer Sci., <u>28</u>, 537 (1958).
- 14. D.E. Winkler, J. Polymer Sci., 35, 3 (1959).
- 15. R.R. Stromberg, S. Straus & B.G. Achhammer, J. Polymer Sci., <u>35</u>, 355 (1959).
- 16. A. Guyot, J.P. Benevise, J. App. Polymer Sci., <u>6</u>, 98, 489 (1962)

The second second

17.	A. Guyot & J.P. Benevise & Y. Tranbouse, J. App. Polymer Sci., <u>6</u> , 103, (1962).
18.	A. Guyot & Pham Queng Tho., J. Polymer Sci., <u>C4</u> , 299 (1964)
19.	W.I. Bengough & H.M. Sharpe, Die Makromolek. Chem., <u>66</u> , 31 (1963)
20.	C.S. Marvel & E.C. Horning in "Organic Chemistry, An Advanced Treatise" Editor Henry Gilman, Vol. I, Second Edition, p. <u>754</u> , John, Willey, 1943.
21.	R.F. Boyer, J. Phys. Colloid Chem., <u>51</u> , 80, (1947).
22.	D.J. Cram & G.S. Hammond "Organic Chemistry", McGraw-Hill, London, 1959, p. 394.
23.	E. Tsuchida, C.N. Shin, I. Shinohara & S. Kambara, J. Polymer Sci.,A2, 3347 (1964).
24.	A.A. Berlin, Doklady Akad. Nauks.S.S.S.R., <u>144</u> , 1042 (1962).
25.	J.P. Roth, P. Rempf & J. Parrod, Compt. Rend. <u>251</u> , 2970 (1960)
26.	I. Ouchi, J. Polymer Sci., <u>A,3</u> , 2685 (1965).
27.	<ul> <li>D.H.R. Barton &amp; K.E. Howlett, J. Chem. Soc. (London) 155, 165 (1949).,</li> <li>D.H.R. Barton, J. Chem. Soc. (London) 148 (1949).,</li> <li>D.H.R. Barton &amp; P.F. Onyon, Trans. Faraday Soc., 45, 725 (1949), J. Amer. Chem. Soc., 72, 988 (1950).</li> <li>K.E. Howlett, J. Chem. Soc. (London) 3695, 4487 (1952)</li> </ul>
28.	V.W. Fuchs & D. Louis, Die Makromolek. Chem. 22, 1 (1957).
29.	C.H. Bamford & D.F. Fenton, Polymer 63, (1969)
30.	J.J.P. Staudinger, Plastic Progress 9, (1953)
31.	H.V. Smith, Rubb. J. Int. Plast., <u>138</u> , 966 (1960)
32.	A. Crosato-Arnaldi, G. Palma, E. Peggion, and G. Talamini, J. App. Polymer Sci., <u>8</u> , 747 (1964)

- 21 -

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( <sub>1</sub>,

- 33. G. Talamini and G. Pezzin, Die Makromolek. Chem. <u>39</u>, 26 (1960).
- 34. B. Braun, M. Thallmaier, Kunstoffe, <u>56</u>, 80 (1966); IUPAC Inter. Symp. Makromole. Chem. Prague (1965) p. 279.
- 35. C.F. Bersch, M.R. Harvey & B.G. Achhammer, J. Res. N.B.S., <u>60</u>, 481, (1958.)
- 36. Z.V. Popova, N.V. Tikhova, and G.A. Razuvaev, <u>Vysomolekul</u>, <u>Soedin</u>, <u>7</u>, 531 (1965).

37. M. Asahina and M. Onozuka, J. Polymer Sci., <u>A</u>,<u>2</u>, 3505, 3515 (1964).

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# CHAPTER II

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# PREPARATION AND CHARACTERIZATION OF EXPERIMENTAL SAMPLES

#### II-1. PREPARATION OF PVC SAMPLES

Four samples of polyvinyl chloride of varying structures were used in the current study. They are designated as PVC-A, -B, -C, and -D.

#### II-1-1. PVC-A

PVC-A was a commercial sample, supplied by Shawinigan Chemicals Limited. The vinyl chloride monomer was polymerized by using benzoyl peroxide as an initiator at 50<sup>°</sup>C. The polymer was isolated by drying the reaction mixture under nitrogen gas. Before using the sample in degradation studies, it was shaken and washed with methanol, filtered and dried in a vacuum desiccator.

This sample contained no additives and was used in the powder form.

### II-1-2. PVC-B

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PVC-B was a linear syndiotactic polymer prepared at low temperature, using tri-isobutylboron as an initiator. The method of preparation was that of Caraculacu<sup>(1)</sup>.

A calculated amount of vinyl chloride was distilled into a pyrex ampoule which was connected to a vacuum line. After distillation of the monomer, the ampoule was disconnected from the system, cooled in a dry

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ice-methanol mixture, swept with helium, and the desired amount of initiator was added. A small amount of air was also introduced in order to accelerate the polymerization reaction. Finally, the ampoule was sealed and kept at  $-43^{\circ}$ C. for 9.5 days.

The polymer was isolated by pouring the reaction mixture into ice-cold methanol. It was then filtered, washed and dried in a vacuum desiccator.

The purification of the sample was effected by swelling the polymer in 1,2-dichloroethane and precipitating it with petroleum ether. After a second precipitation, it was dried in a vacuum desiccator.

II-1-3. PVC-C

PVC-C was a polyvinyl chloride sample containing tertiary hydrogen atoms. This functionality was introduced by copolymerizing vinyl chloride with l-chloropropene.

The methods of preparation, isolation and purification were the same as described for PVC-B.

#### II-1-4. PVC-D

PVC-D was a polyvinyl chloride containing tertiary chlorine atoms and was prepared by copolymerizing vinyl chloride with 2-chloropropene.

The methods of polymerization, isolation and

purification were the same as that described for PVC-B and PVC-C.

The experimental conditions used in the preparation of all samples are given in Table II-1.

II-1-5. Materials

The tri-isobutyl boron, 1-chloropropene and 2-chloropropene were obtained from K and K Laboratories, Inc., and vinyl chloride was obtained from the Matheson Gas Co.

### II-2. CHARACTERIZATION OF PVC SAMPLES

#### II-2-1. Molecular Weight Measurements by Osmometry

The number average molecular weights,  $\overline{M}_n$  were measured by means of a High Speed membrane Osmometer, using cyclohexanone as a solvent.

The basic relation for the calculation of molecular weight is

$$\left[\Pi/c\right]_{c=0} = \frac{RT}{M_n} \qquad (II-1)$$

where II = osmotic pressure c = concentration in g/l R = gas constant T = absolute temperature

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# TABLE II-1

# EXPERIMENTAL CONDITIONS USED IN POLYMERIZATIONS

Sample	Initiator	Wt. % of Initiator	Temp. °C	Time	Yield %	Monomer Feed Ratio VC/PC
Δ	Bz O					
л	<sup>B2</sup> 2 <sup>O</sup> 2	0.04	50	15.5 hrs.	6.2	-
В	TIBB	1.5	-43	19.5 days	6.1	-
C	TIBB	1.1	-43	21.5 days	2.3	2.95/1
D	TIBB	1.1	-43	16.5 days	2.0	0.52/1
Bz202	: В	enzoyl Peroxi	de			
TIBB	: т	ri-isobutyl b	oron			· ·
VC	: V	inyl chloride	monomer			
PC	: 1	-Chloropropen	e for PV	C-C ; 2-Chl	oroproper	ne for PVC-D
Bz2 <sup>0</sup> 2 TIBB VC PC	: B : T : V : 1	enzoyl Peroxi ri-isobutyl b inyl chloride -Chloropropen	de oron monomer e for PV	C-C ; 2-Chl	oroproper	ne for

Since the value of I/c is a function of the concentration, the extrapolated value of I/c at zero concentration,  $(I/c)_{c=0}$ , in the plot of I/c vs. c, is used in the above relation.

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The gas constant, 'R', for a pressure of cyclohexanone was calculated to be

> 92.77 liter cm. of cyclohexanone degree<sup>-1</sup>mole<sup>-1</sup>, - at 60<sup>o</sup>C. 95.14 liter cm. of cyclohexanone degree<sup>-1</sup>mole<sup>-1</sup>, - at 85<sup>o</sup>C.

The molecular weights of the polystyrene standard samples, obtained from Water Associates, also measured in cyclohexanone solution, are given below.

#### TABLE II-2

MOLECULAR WEIGHTS OF STANDARD SAMPLES

Polystyrene Sample No.	Temp. o C	M <sub>n</sub> given	M <sub>n</sub> measured	Difference	Error in %
4190041	60	4.9x10 <sup>4</sup>	5.166x10 <sup>4</sup>	2.6x10 <sup>3</sup>	5.3
41984	85	1.64x10 <sup>5</sup>	1.702x10 <sup>5</sup>	6.2x10 <sup>3</sup>	3.7

On the basis of the above, the error in determin-

ation of  $\overline{M}_n$  for the samples used in the degradation studies can be assumed to be ± 5%.

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The molecular weights measured for samples PVC-A, -B, -C and -D, are given in Table II-3.

#### TABLE II-3

MOLECULAR WEIGHTS OF EXPERIMENTAL PVC SAMPLES

Sample	™ <sub>n</sub>	Temp. <sup>O</sup> C.
PVC-A	54,196	60
PVC-B	75,666	85
PVC-C	27,909	85
PVC-D	36,776	60

# II-2-2. <u>Measurement of Glass Transition</u> <u>Temperatures</u>

Glass transition temperatures of all samples were measured, using a Perkin Elmer Differential Scanning Calorimeter Model D.S.C. 1-B. The temperature scanning rate used was 5°C./minute. The results obtained are given in Table II-4.

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### TABLE II-4

Sample	<sup>T</sup> g °c.
PVC-A	86
PVC-B	87
PVC-C	84
PVC-D	84

GLASS TRANSITION TEMPERATURES,  $T_{q}$ , OF PVC SAMPLES

Since the error in the  $T_g$  value obtained by D.S.C. is  $\pm 3^{\circ}$  C., there is no significant difference in the observed values.

# II-2-3 Measurement of % Crystallinity

The % crystallinity of the PVC samples were measured on an x-ray diffractometer. The machine used was a "Rich-Seifert & Co." G.M. Counter x-ray diffractometer.

Powdered PVC samples were placed on specimen holders which were then mounted on a rotating table. Cu Ka radiation was used, and the scattered radiation was detected by a Geiger counter, connected to a pen recorder read out. Samples were rotated from  $2\theta = -4^{\circ}$ 

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to 40°. The area under the peaks were measured and the percentage crystallinities were obtained by the method reported in the Dow Chemical Research Report, for the relative % crystallinity in polypropylene<sup>(2)</sup>. Standard samples of quartz powder and polypropylene were measured under similar conditions in order to calibrate the machine. The results obtained are given in Table II-5.

#### TABLE II-5

Sample	<pre>% Crystallinity</pre>	Relative Crystallinity
PVC-A	27.5	1
PVC-B	47.4	1.7
PVC-C	60.8	2.2
PVC-D	36.4	1.3

#### CRYSTALLINITY OF EXPERIMENTAL PVC-SAMPLES

# II-2-4 Copolymer Compositions

To calculate the mole % of propenyl chloride in the various copolymers, the following relationship, given by Caraculacu<sup>(1)</sup>, was used.

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$$N_{1} = \frac{100}{1.225 \left\{ \frac{E_{1} - E_{2}}{E_{1} - E_{2}} \right\} - 0.255}$$
(II-2)

where

E<sub>1 & E<sub>2</sub> = gravimetric % of chlorine in chloropropene and vinyl chloride monomers, respectively.</sub>

In determinations based on homopolymer chlorine content, a small systematic difference between chlorine content of the monomer and that of the homopolymer has been observed  $^{(3,4)}$ . This systematic error is corrected by applying a correction to  $E_2$  and using the corrected value  $E'_2$  in calculation. This  $E'_2$  correction was estimated by the chlorine analysis of homopolymer PVC-B. The relation (II-2) then becomes

$$N_{1} = \frac{100}{1.225 \left\{ \frac{E_{1} - E_{2}^{\dagger}}{E_{1} - E_{2}^{\dagger}} \right\} - 0.225}$$
(II-3)

Using the above equation, the copolymer compositions shown in Table II-6 were calculated.

#### TABLE II-6

Sample	C\$	H\$	C1%	Propenyl Chloride in Copolymer, in mole %
B	39.37	5.10	55.09	0
С	40.00	5.03	54.14	9
D	40.23	4.81	54.43	6

COPOLYMER COMPOSITION OF PVC-C AND PVC-D

# II-2-5 Determination of 1,2,dichloride units in Experimental Samples

In order to determine the regularity of the head to tail configuration in PVC samples, the content of 1,2, dichloride units in the samples was determined by the potassium iodide method (5,6). The 1,2, dichloride unit liberates free iodine in the following manner, when it is treated with potassium iodide.

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 $\begin{array}{cccc} R-CH-CH-R + 2KI \longrightarrow R-CH-CH-R + 2KC1 & (II-4) \\ I & I & I \\ CI & CI & I & I \end{array}$ 

$$\begin{array}{ccc} R-CH-CH-R & \longrightarrow & R-CH=CH-R + I \\ & I & I \\ & I & I \end{array}$$
(11-5)

- 32 -

About 0.2 - 0.25 g. of sample and 1.0 g. of potassium iodide were placed in glass ampoules, with 15 c.c of peroxide free dioxane. The contents of the tube were thoroughly degassed and then sealed under vacuum. The samples were then heated at boiling water temperature for four days. The ampoules were then cooled, and the reaction mixtures were poured into a chloroform and water mixture (1:5). One c.c of starch solution was then added and the free iodine was titrated with standard sodium thiosulphate solution.

None of the experimental samples exhibited a colour change on the addition of starch solution. Thus, the 1,2, dichloride unit is absent and the samples are concluded to be essentially of the head to tail configuration. The absence of the 1,2, dichloride units allows us to assign the following structures to PVC-C and -D.

$$\frac{PVC-C}{CH_2} - CH_2 - CHC1 - \frac{H}{CH_3} - CHC1 - CH_2 - CHC1 - CH_2 - CHC1 - CH_3 - CHC1 - CH_3$$

$$\underline{PVC-D} -CH_2 - CHCl - CH_2 - CHCl - CH_2 - CHCl - CH_2 - CHCl - CH_3 - CHCL - CH_3$$

### II-2-6 Determination of Syndiotacticity and Branching in the Experimental Samples

The ratio of syndiotactic to isotactic units in

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PVC has been found to be related to the ratio of absorbance at 635 cm<sup>-1</sup> to that at 692 cm<sup>-1</sup> in the IR spectra<sup>(7)</sup>. Nakajima, Hammadi and Hayashi<sup>(8)</sup>, have compared the degree of branching and syndiotacticity of PVC samples prepared from 90°C. to  $-75^{\circ}$ C., and their results are shown in Table II-7.

#### TABLE II-7

SAMPLES PREPARED FROM 75 C CO 50 CT					
Samples	Method of Preparation	Temp <sup>O</sup> C	Degree of Branching CH <sub>3</sub> 100CH <sub>2</sub>	Syndio- tacticity	
1	Bulk-Bz202	90	0.27	0.51	
2	Com-Geon 103ED	55-60	0.20	0.53	
3	Com-Geon 103ED	50	0.20	0.54	
4	Com-Geon 103ED	-15	0.05	0.64	
5	Photopolym. Uranyl NO <sub>3</sub>	-75	0.00	0.77	

DEGREE OF BRANCHING AND SYNDIOTACTICITY OF PVC SAMPLES PREPARED FROM -75°C to 90°C.<sup>(8)</sup>

Table II-7 suggests that PVC-B, which is prepared at  $-43^{\circ}$ C., has less branching and exhibits a more syndiotactic character than PVC-A which was prepared at 50°C. The ratios of the infrared absorptions at  $635 \text{ cm}^{-1}$  to  $692 \text{ cm}^{-1}$  for these two samples, (Table II-8),

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2.1 for PVC-A and 3.6 for PVC-B support this contention. Furthermore, on the basis of Nakajima's data, it can be assumed that PVC-A, which is similar to sample 1 and 2, in the above Table, will have a branch after every 400 CH<sub>2</sub> units, while the low temperature samples 4 and 5, and B in the present studies, will have less branching.

The properties of all samples used in the present experiments are summarized in Table II-8.

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# TABLE II-8

# PROPERTIES OF EXPERIMENTAL POLYVINYL CHLORIDES

Sample	C %	Н 8	Cl %	Propenyl Chloride in Copolymer mole %	$\frac{A_{635 \text{ cm}}^{-1}}{A_{692 \text{ cm}}^{-1}}$	(a) T oC	(b) M <sub>n</sub>	Relative Crystallin- ity	Structure
A	37.96	4.95	56.44	-	2.1	86	54,196	1	regular
В	39.37	5.10	55.09	-	3.6	87	75,666	1.7	linear
с	40.00	5.03	54.14	9	-	84	27,909	2.2	tertiary H
D	40.23	4.81	54.43	6	-	84	36,776	1.3	tertiary Cl

(a)  $\pm 3^{\circ}C$ .

(b) ± 5%.

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#### II-3. REFERENCES

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#### CHAPTER II

1. A. Caraculacu, J. Polymer Sci. Al, 4, 1829 (1966) 2. Dow Chemical Research Report SL.87902, "Relative % Crystallinity in Polypropylene". 3. H. Staudinger & J. Schneiders, Ann, 541, 151 (1949). 4. H. Staudinger & M. Haberle, Die Makromolek. Chem., 9, 151 (1953). 5. F.R. Mayo & K.E. Wulzback, J. Amer. Chem. Soc. 71, 1124 (1949). 6. C.S. Marvel, J.H. Sample & M.F. Roy, J. Amer.Chem. Soc. 61, 3241 (1939). J.W.L. Fordham, P.H. Burleigh & C.L. Sturm, 7. <u>J. Polymer Sci., 41</u>, 73 (1959) 8. A. Nakajima, H. Hamada & S. Hayashi, Die Makromolek.

8. A. Nakajima, H. Hamada & S. Hayashi, <u>Die Makromolek</u>. <u>Chem</u>. <u>95</u>, 40, (1966).

# CHAPTER III

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# EXPERIMENTAL TECHNIQUES

#### EXPERIMENTAL TECHNIQUES

Two methods for the determination of the thermal stability of PVC samples have been employed in the present study:

- A. Thermogravimetric Analysis.
- B. E.S.R. HCl evolution measurements.

#### III-1 THERMOGRAVIMETRIC ANALYSIS

#### III-1-1. Introduction

Thermogravimetric methods are widely used in the determination of polymer stabilities and a number of papers and reviews have been published (1-7) on this technique. In this method, the samples are continuously weighed on a microbalance while being heated. Weight losses can then be calculated against heating times or against the temperature of heating. The T.G.A. methods can be divided into two classes:

#### (i) Isothermal or Static Thermogravimetry

In this method, the weight changes of the sample are recorded with the time of heating at constant temperature.

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#### (ii) Dynamic Thermogravimetry

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In this method, the weight changes are measured while the sample is undergoing a programmed temperature change.

In the present work, the dynamic TGA method was adopted and the measurements were performed on an apparatus which included a CAHN electro balance Model R.G. (Fig. III-1).

The electrobalance had two suspension loops, A and B for small and large amounts of the samples, respectively. The specifications for these loops are given below:

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Loop B

Maximum Load	l g.	2.5 g.
Maximum change in weight	100 mg.	1000 mg.
Sensitivity	10 <sup>-7</sup> g.	5x10 <sup>-7</sup> g.

In the present study, Loop A was used.

Loop A

# III-1-2 Size and Shape of the Samples

In the TGA of polymers the shape and the size of a sample plays an important role, since the diffusion of degradation products through the polymer

# FIGURE III-1

# APPARATUS FOR THERMOGRAVIMETRY

A,B,C	: WEIGHING LOOPS
D:	TO GAS INLET (N <sub>2</sub> VIA MANOMETER)
E:	TO VACUUM LINE.
F:	STOP COCK
G:	GLASS CHAMBER

- H: CAHN BALANCE
- I: SAMPLE PAN
- J: PAN FOR COUNTER WEIGHTS



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mass changes the rate of weight loss. Vasallo<sup>(8)</sup> studied the effect of the thickness of the film on the weight loss behaviour of "Moplen M/2" polypropylene. His results showed the expected result, that thinner samples lost weight more rapidly than the thicker ones, and that in order to reproduce results within  $\pm 2$ %, the 10 mil thickness had to be controlled to 0.1 mil or less.

In early experiments in the present work, polymer pellets of 5 to 8 mils made by compacting powder were used. The results were not reproducible, however, since the degradation of pellet samples were found to be dependent on the pressure used in pressing the pellets. When unpelleted powder samples of 40-60 mesh were used, the results were highly reproducible. Particles of this size range were therefore used throughout the remainder of the experimental work.

# III-1-3 Atmosphere

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It has been shown that the presence of a sizeable gas pressure in the reaction tube can affect the weight loss behaviour of the samples (8). In the present studies, in order to circumvent this difficulty, the whole weighing assembly was evacuated at the commencement of each run and then a small, constant flow of nitrogen was maintained during evacuation, to give a reduced pressure which was measured by a manometer. This N<sub>2</sub> flow

was then continued during the degradation experiments.

#### III-1-4 Technique

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The glass sample pan was suspended from the loop A and the zero control and recorder range were calibrated according to the instruction manual of the instrument. In order to study the pyrolysis in reduced pressure, a specially designed hang down tube was used (Fig. III-1). The flow of nitrogen gas was introduced through D (Fig. III-1), and a mixture of carrier gas  $N_2$ , and the HCl gas, generated from the sample, was swept out by applying vacuo from the bottom of the tube at E. In this manner, the corrosive HCl gas was kept away from the balance chamber. The temperature was measured by a chromel-alumel thermocouple, placed just below the sample pan.

About 40-60 mg. of a powdered PVC sample, of 40-60 mesh was placed in a glass sample pan. The envelope containing the microbalance was then evacuated from the outlet of the hang down tube E. After evacuation, the vacuum gate was closed and the whole assembly was flushed with high purity  $N_2$  gas. After four such evacuations - flushing cycles, the system was again evacuated and a small metered flow of nitrogen was maintained. This flow yielded a reduced pressure of  $N_2$  of any desired value. The pyrolysis furnace was preheated to  $35^{\circ}$ C. and the hang down tube was inserted into it by elevating a jack under the furnace. When the temperature of the sample (as recorded by thermocouple) became constant, the temperature was programmed at a rate of increase of  $5^{\circ}$ C/min. The sample weights were recorded on the lmV L & N recorder. After each minute the temperature was measured by thermocouple, and was noted on the recorder chart paper, along with the sample weight. The heating was continued until the temperature had reached  $350-400^{\circ}$ C., at which time the furnace was removed.

A correction for the weight in reduced pressure and weight in air was applied. A blank run, sample pan only, was also made under similar conditions to those used in the run. A straight base line was obtained.

An instrumental sensitivity of  $\pm 0.1$ % in the weight change was applied to all of the thermogravimetric measurements.

Duplicate runs on the same PVC sample were made, and the results were found to be reproducible within  $\pm$  2%. The experimental conditions, such as heating rate, flow of N<sub>2</sub> etc., were kept constant throughout all of the thermogravimetric measurements.

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# III-2 E.S.R. AND HC1 MEASUREMENTS

III-2-1. Introduction

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The E.S.R. measurements were performed on a Varian Model 4500-10A E.P.R. spectrometer. The powdered polymer samples were placed in a tube and heated inside the cavity of the instrument. The samples were degraded in a nitrogen stream which also acted as a carrier gas for HCl generated from the polymer. The exit gas, carrying the HCl, was then bubbled through conductivity water contained in a conductivity cell. Conductivity measurements were made at 25°C. on an Industrial Instruments RC-18 conductivity bridge and were used to define the rate of the HCl evolution.

In order to get a uniform packing of the sample in the tube, the polymer was first heated, for a very short time, above the glass transition temperature (84-87<sup>o</sup>C.), after which the temperature was increased to that desired for the decomposition experiment. The spin formation and HCl generation were determined from the E.S.R. signal and conductivity measurements, respectively.

# III-2-2 HCl Measurement

In the degradation of PVC below 250<sup>o</sup>C., hydrochloric acid gas is the main product. The evolved HCl gas can be measured in a number of ways, such as acid base titra-

- 44 -
tion, Argentometric titration and conductometric measurements. In the present work, where the evolved gas was swept from the sample chamber and bubbled through conductivity water in a conductivity cell, the change in the conductivity was correlated with the concentration of the acid.

The conductivity cell used in the present study was a dip type, obtained from the Fisher Scientific Co., (Cat. #9-382), and had a cell constant of 0.112 reciprocal cm. The area of the platinum electrodes was 3.1 cm<sup>2</sup>.

The cell was dipped inside the conductivity water, contained in a specially designed vessel, having three inlets. Inlet 'A' was used to insert the conductivity cell, 'B' as the inlet for HCl +  $N_2$  and 'C' was used as an exit. The whole vessel was immersed in a thermostated bath at 25°C. The conductivity water was stirred by means of a magnetic stirrer. The resistance of the cell was measured on an Industrial Instrument conductivity bridge Model RC 18. The exit gas from the cell, was bubbled into another vessel containing conductivity water, in order to check the presence of HCl in the exit gas. The absence of HCl gas was confirmed by measuring the conductivity of the second solution. The conductivities at 25°C., of standard HCl solutions of normalities ranging from 6 x  $10^{-4}$  to 122.0 x  $10^{-4}$ , were measured, using the above instrument. A calibration curve for 1/R vs.  $\sqrt{C}$ , where R is resistance in ohm and C is the concentration of HCl solution in

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moles/1, was constructed (Fig. III-2). This calibration curve was used to calculate the moles of HCl present per liter of solution.

The estimated error in the measurement of HCl was  $\pm$  5%. Duplicate runs were made and the overall reproducibility in the measurement of the rate of HCl evolution was found to be within 8 to 10%.

#### III-2-3 Spin Measurements

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Degraded PVC samples have been found to give an E.S.R. signal at even very low stages of degradation<sup>(12)</sup>. In the present study, the intensity of the E.S.R. signal was correlated with the heating times.

The minimum measurable spin concentration of the instrument at the time of installation was  $1 \times 10^{11}$  spins. With the continuing use of the instrument, this sensitivity diminished and therefore, in every set of experiments a control (Blank PVC-A) was run.

In the present work spin concentrations were measured by the comparison method. In this method, the spin concentration of unknown samples were measured relative to a standard sample of known spin concentration. The number of spins in any sample is proportional to the area under the absorption curve

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### FIGURE III-2

CALIBRATION CURVE FOR THE MEASUREMENT OF

HC1 CONCENTRATION BY CONDUCTIVITY METHOD.

R = RESISTANCE IN OHMS OBTAINED IN CONDUCTIVITY
CELL.

C = CONCENTRATION OF HCl IN MOLES/LITER.

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N = KA (III-1)

where N = # of spins,

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K is an instrument constant depending upon amplifier gains, modulation amplitude and microwave power, etc.,

A = area under the absorption curve.

Andrews<sup>(10)</sup> and Burgess<sup>(11)</sup> have shown the equivalence between the area under the absorption curve and the first moment of the first derivative curve, which is obtained from the E.S.R. instruments. Therefore, (III-1) can be written as

N = KM (III-2)

where, M is the first moment of the first derivative curve.

If  $N_1 K_1$  and  $M_1$  refer to Sample 1, and  $N_2 K_2$  and  $M_2$  are for Sample 2, then

$$N_1 = K_1 M_1$$
 (III-3)

$$N_2 = K_2 M_2 \qquad (III-4)$$

If the experiments for both samples were run under similar conditions, then

$$K_1 = K_2 \qquad (III-5)$$

Substituting in Equation (III-4) for K<sub>2</sub>

$$N_2 = K_1 M_2$$
 (III-6)

and

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$$\frac{N_1}{N_2} = \frac{M_1}{M_2}$$
 (III-7)

or

$$N_1 = N_2 \times \frac{M_1}{M_2}$$
 (III-8)

By using a standard sample of some stable free radicals, whose spin concentration can be known from some independent method,  $N_1$  is calculated.

In the present work, 1,1' diphenyl-2-picryl hydrazyl (DPPH) was used for the comparison of spin concentration.



DPPH is a stable free radical at room temperature provided it is kept sealed in an inert atmosphere, and stored in the dark. A freshly crystallized sample of DPPH,from benzene solution, was used in the present work. A concentrated solution of DPPH was made by dissolving DPPH in benzene and the desired concentrations of solutions were obtained by dilution with solvent.

The concentration of DPPH in dilute solutions

were determined by spectrophotometry. The value of the molar absorbance of DPPH in benzene at 517 m  $\mu$  was obtained experimentally and has been used throughout the calculations.

With the DPPH solution as a standard in the calculation of spin concentration, an experimental error of  $\pm$  10% is to be expected<sup>(12)</sup>.

The  $\frac{d \text{ spin}}{dt}$ , that is the slope of the spin-time curve, was reproducible within 8 - 10%.

### III-2-4. Measurement of 'g' values

The g value, the spectroscopic splitting factor, of any E.S.R. spectrum is related to the nature of the species from which the signal is obtained. Free radicals have a g value very close to 2,(2.0023), while transition elements and metallic ions have g values higher than 2.

When a material containing an unpaired electron is placed in an external magnetic field, the energy level of the electron is separated into two new levels which can be depicted as follows

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at resonance

 $h_V = g\beta H$  (III-9)

where

h = Planks Constant
ν = frequency of radiation emitted
g = spectroscopic splitting factor
H = Field of Resonance
β = Bohr magneton

In the above relation 'g' is the dimensionless, spectroscopic splitting factor, and is a physical property of the unpaired electron. This constant is used to define the position of peaks in an E.S.R. spectrum. If an electromagnetic radiation of frequency  $\vee$  is now applied to the sample, some of the electrons in the lower state will absorb energy and jump to a higher energy state.

At the same time, the electron from upper energy state will emit radiation of  $\vee$  frequency and fall to the lower energy state. Electron resonance absorption can take

place at any frequency provided the magnetic field is adjusted to satisfy the relation.

$$hv = g\beta H$$
 (III-9)

The 'g' values of signals are measured as follows:

The spectra of the samples are compared with the spectra obtained from a standard compound, in the present work, potassium nitrososulphonate. A dilute solution of this salt in water containing sodium carbonate was prepared. It was then sealed in a thin wall capillary tube and was stored. This sample was found to be stable if preserved under refrigeration. Defining the standard sample relationship (III-9) as

$$hv_{g} = g_{g}\beta H_{g}$$
 (III-10)

and for the unknown sample.

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$$hv_{\mu} = g_{\mu}\beta H_{\mu} \qquad (III-11)$$

where the subscripts s and u indicate the values for standard and unknown samples.

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Dividing (III-11) by (III-10)

$$g_{u} = \frac{v_{u}}{v_{s}} g_{s} \frac{H_{s}}{H_{u}}$$
(III-12)

Since the experiment was done in a dual cavity . equation (III-12) reduces to

$$g_u = g_s \frac{H_s}{H_u}$$
 (III-13)

The spectra of PVC and standard samples, measured using the dual cavity, were recorded on two pen recorders. The pattern obtained is shown in Fig. III-3.

In Fig. III-3, the standard sample showed three signals equally separated by 13 Gauss. The 'g' value of this signal was 2.0055. The chart speed of recorder was calibrated by using the distance between first and third peaks and 'g' values of the spectra of PVC were calculated as follows:

If the distance between the first and the third peak is 'a' cm, the field of resonance for potassium nitrososulphonate spectra is  $H_g$  and the distance between the resonance of unknown and known signal is 'b' cm, then

$$a cm = 26 Gauss$$
 (III-14)

$$l cm = \frac{26}{2} \qquad (III-15)$$

$$b \ cm = \frac{26}{a} \ x \ b \ Gauss$$
 (III-16)

Therefore, the resonance for unknown will be

$$H_u = H_s + \frac{26 b}{a}$$
 Gauss (III-17)

Substituting in (III-13),  $g_u$  can be evaluated.

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## FIGURE III-3

CALCULATION OF 'g' VALUE.

(-----) SIGNAL OBTAINED FROM STANDARD COMPOUND SOLUTION.

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(----) UNKNOWN SIGNAL.

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$$g_{u} = \frac{2.0055 \times H_{s}}{(H_{s} + \frac{26 \text{ b}}{2})}$$
(III-18)

In the calculations of 'g' for the E.S.R. spectra obtained on heat-treated PVC samples, a correction for recorder pen errors was also applied, and the 'g' values with their respective errors are reported.

#### III-3. REFERENCES

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#### CHAPTER III

- A.W. Coates & J.P. Redfern, The Analyst <u>88</u>, #1053 p. 906 (1963).
- 2. D.A.Anderson & E.S. Freeman, J. App. Polymer Sci., <u>1</u>, 192 (1959), <u>Nature</u> 195, 1297 (1959), <u>J</u>. Polymer Sci. <u>54</u>, 253 (1961).
- 3. D.A. Anderson, J. App. Polymer Sci. <u>6</u>, 484,(1962).
- 4. E.S. Freeman & B. Carrol, J. Phys. Chem., <u>62</u>, 394 (1958)
- 5. A.E. Newkirk, J. Amer. Chem. Soc., <u>77</u>, 4521 (1955), Analytical Chem. <u>32</u>, 1558 (1960).
- A.E. Newkirk & I. Aliferis, Analytical Chem. <u>30</u>, 982 (1958).
- 7. C.D. Doyle, J. App. Polymer Sci., <u>5</u>, #15, 285 (1961) J. App. Polymer Sci., <u>6</u>, #24, 639 (1962)
- 8. D.A. Vassallo, Analytical Chemistry 33, 1823 (1961).
- 9. I. Ouchi, Prog. in Polymer Physics, in Japan, Vol. VIII (1965) 367.
- 10. E.R. Andrews, Physical Rev. <u>91</u>, 425 (1953).
- 11. V.R. Burgess, J. Sci., Instruments <u>38</u>, 98 (1961).
- 12. K.M. Mausser, Rad. Research Supplement, 2, 480 (1960)

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## CHAPTER IV

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# MECHANISM OF THERMAL DEGRADATION

### OF

# POLYVINYL CHLORIDE

# MECHANISM OF THERMAL DEGRADATION OF PVC

#### IV-1 INTRODUCTION

In this Chapter the difficult task of determining a reaction mechanism in a solid state is undertaken.

Through the data derived from simultaneous HCl and spin generation measurements on polymers containing known quantities of built-in structural irregularities, rates and energetics for two of the steps in the decomposition reaction have been defined. In the treatment of the spin data, we have not been able to determine reaction order, but have had to resort to a rate determination based on simply plotting concentrations against times, and taking the slopes of that relationship. It has been possible however, to treat the HCl data in a more conventional manner.

In the end, we propose a reaction path for PVC degradation which allows one to predict the effects of structural irregularities on polymer stability.

Despite the fact that the complexity of the system has not always allowed the use of classical kinetic treatment, the results obtained are thought to be sufficient justification for the experimental path taken.

#### IV-2 THERMOGRAVIMETRY

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The thermograms obtained on the degradation of four experimental samples are shown in Figure IV-1.

In interpreting these curves, any one of three methods is commonly used. In the first, the slope of the curves at any temperature can be utilized as a measure of stability, since it is directly proportional to the rate of weight loss. The shape of the curve will depend on nearly all of the experimental conditions, including the heating rate, the shape and the size of sample, the type of sample holder, the atmosphere in which the decomposition is taking place, etc. Thus, only if all experiments are carried out under exactly the same conditions, can the slopes of the curves at any temperature be used as a direct measurement of the comparative stabilities.

A second method which is often utilized is the comparison of the temperatures at which the decompositions commence  $^{(1)}$ . This would be the temperature at which the base line in the thermogram undergoes a marked deviation. This method is not favoured in that, in addition to depending upon the variables stated in the previous paragraph, it may also be influenced by small quantities of impurities, with the result that the deviation temperature may not be related to the onset of the degradation of the major portion of the sample.

# FIGURE IV-1

RELATIVE THERMAL STABILITY OF PVC SAMPLES BY DYNAMIC THERMOGRAVIMETRY.

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(O) PVC-A, (X) PVC-B, ( $\Delta$ ) PVC-C, ( $\Box$ ) PVC-D

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A third method, utilized by Pellon<sup>(2)</sup> and which circumvents the problems of the latter method, uses the temperature  $T_{10}$ , the temperature at which the cumulative weight loss has reached 10% of the infinite time weight loss. In the present study, we have adopted this procedure. These values for all four samples, derived from Fig. IV-1, are given in Table IV-1.

TABLE IV-1

Samples	<sup>T</sup> 10 °C	Structure		
PVC-A PVC-B PVC-C PVC-D	294.5 301.0 247.0 281.5	Regular Linear Tertiary-H -C- CH <sub>3</sub> Cl Tertiary-Cl -CH <sub>3</sub> CH <sub>3</sub>		

T<sub>10</sub> VALUES FOR PVC-A, B, C, D.

The Table reveals that the thermal stabilities of the PVC samples in terms of  $T_{10}$  are in the following order:

PVC-B > PVC-A > PVC-D > PVC-C

This order suggests that

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a. linearity of structure improves stability.

b. branching of any kind decreases stability.

If this order is assumed to be associated with the initiation of degradation, it is in agreement with the findings of Asahina & Onozuka<sup>(3)</sup>, who, using model compounds, observed tertiary chlorides to undergo more rapid thermal degradation than the secondary and to exhibit activation energies for decomposition 30 to 40 kcals/mole less than those for the secondary structures. Some of their results are shown in Table IV-2.

#### TABLE IV-2

#### ACTIVATION ENERGIES FOR THE

Compound K	E cal/mole	
2-chloropropane	42.4	
2,4-dichloropentane	69.9	
2-methyl-2-chloropropane	41.6	

DEHYDROHALOGENATION OF MODEL COMPOUNDS (3)

The stability comparison in the present samples, while useful, does not shed a great deal of light on the degradation mechanism when one considers the complexity of the processes involved in the polymer breakdown. Simple HCl evolution rates give little or no information concerning the rates of initiation and termination of degradation and no information, whatsoever, on the chain lengths for the HCl ejection. A more complete understanding is possible, if the number of propagating chains are monitored during the course of the HCl evolution. Accordingly, preliminary measurements were made by means of electron spin resonance to determine whether or not the behaviour of the radicals generated thermally could be related to the rate of HCl evolution.

## IV-3 PRELIMINARY SIMULTANEOUS MEASUREMENTS OF E.S.R. AND HCL EVOLUTION.

A number of workers have reported the presence of radicals in irradiated (4-8), and heat-treated (9)PVC. In the present work, it was deemed necessary to determine whether these radicals are indeed related to the decomposition or are simply a by-product thereof. To accomplish this, a simple thermal decomposition of PVC-A was performed in the core of the E.S.R. machine, and rates of HCl evolution and spin generation were measured simultaneously. The results are plotted in Fig. IV-2. In this figure, the HCl evolution is plotted on the left ordinate and spin generation on the right. It is seen that there is indeed a relationship between HCl evolution and spin generation. This observation was considered sufficient evidence to warrant a deeper investigation of this question,

# FIGURE IV-2

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SIMULTANEOUS MEASUREMENTS OF HC1 EVOLUTION AND SPIN GENERATION;

SAMPLE: PVC-A, TEMPERATURE: 233<sup>O</sup>C. REACTION ATMOSPHERE: NITROGEN.

( $\Delta$ ) HCl ON LEFT-HAND AXIS, (O) SPIN ON RIGHT-HAND AXIS.



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since this coincidence could well be related to the various structural entities. Before undertaking such an investigation, however, it was necessary that we have a better understanding of the nature of the radical. The questions which must be answered are associated with the type of the radical , and whether it is a product of the reaction or perhaps a separate entity which is associated with the decomposition.

In an attempt to answer these questions, radicals were generated in the sample by the  $\gamma$  irradiation of PVC at liquid nitrogen temperature, in the manner of Miller<sup>(4)</sup>, and the spectra of these were investigated as a function of time at -78°C. and at room temperature. The behaviour of these radicals were then compared to those which are generated thermally.

### IV-4. DETERMINATION OF THE NATURE OF THE RADICAL SPECIES IN PVC

Miller in 1959<sup>(4)</sup>, studied, by electron spin resonance, the radicals produced in polyvinyl chloride samples by 800 kv electron irradiation. He concluded that on irradiation, the radical  $-CH_2-CH-CH_2-$  was produced. This decayed rapidly at room temperature, in the presence of oxygen.

Atchison, in similar experiments <sup>(5)</sup>, found that three radicals were produced and that these decayed by first

- 64 -

order kinetics with half lives of 4.5, 63 and 1630 hours.

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Ohnishi, Nakajima & Nitta<sup>(6)</sup>, also concluded that several types of radicals were produced. On heating, some of these disappeared. Simultaneously, colour developement was observed. This colour was related to the formation of polyenes, whose appearances were associated with the disappearance of the radicals. Ohnishi, <u>et al</u><sup>(6)</sup> also noted the change in the width of the E.S.R. signal, as the degradation proceeded.

Ouchi in 1965<sup>(9)</sup>, observed the radicals in the heat-treated PVC. In his studies, the PVC sample was heated at a fixed temperature, for different time intervals, and the radicals were measured by recording the E.S.R. spectra of these degraded samples. It was observed that E.S.R. signals appeared at an early stage of dehydrochlorination, and levelled off when the dehydrochlorination was complete. They suggested that the spin formation is related to the dehydrochlorination reaction.

The work done in the past can be summarized as follows. On irradiation PVC gives radicals which decay on heating.

In the present study, detailed E.S.R. measurements were done on only one  $\gamma$ -irradiated sample PVC-A. This is the sample which, in subsequent chapters, was utilized in

- 65 -

measuring the relationship of spin to dehydrochlorination in the presence of oxygen, U.V. initiation, etc.

Polymer sample A was irradiated in a specially designed apparatus Fig. IV-3. The sample was placed in the and the assembly was evacuated to a low wider limb 'A' vacuum for 30 minutes, and then sealed at x. The whole apparatus was then immersed in liquid N, and irradiated by  $\gamma$ -rays, from a Co-60 source, at a dose rate of 4.0 x  $10^5$  rads/hr. The total dose given to the sample was 5 Mrads. After irradiation, the wide tube containing the sample was dipped into liquid N<sub>2</sub> and the empty narrow tube, which was to be inserted into the E.S.R. cavity, was flame annealed to eliminate the paramagnetic centers in the glass. Both the ends of the tube were then cooled, by immersion in liquid N2, after which the whole apparatus was inverted and the sample was shaken into the flamed end of the narrow tube. This tube was then sealed and stored in liquid Nitrogen.

The E.S.R. spectra were measured at liquid  $N_2$ temperature. For this purpose, a low temperature dewar filled with liquid nitrogen was placed inside the E.S.R. cavity. The sample tube was quickly transferred to this dewar and the new spectra were recorded. To determine spin lifetimes, the sample was heated to  $-78^{\circ}$ C. (dry ice + CH<sub>3</sub>OH) for a short time, and then recooled to liquid  $N_2$  temperature for another measurement. Finally, the sample was

- 66 -

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FIGURE IV-3

Apparatus for irradiation of polymer sample.

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brought to room temperature, held for an interval of time, and again cooled to liquid nitrogen temperature for the measurement of the spectra. The spectra obtained are given in Fig. IV-4.

Immediately after the irradiation, the spectrum is observed to exhibit a singlet shape with hyperfine splitting. This behaviour is of a similar nature to the pattern obtained by previous authors (4, 6-8). The pattern is a complex one, and can be divided into two separate signals A and B. (Fig. IV-4). Their width at the maximum slope,  $\Delta$  Hmsl, of the absorption curve, which is a peak-to-peak distance in the first derivative curve; along with their intensities, the peak-to-peak heights were measured. These values are given in Table IV-3, as a function of heating times.

From Table IV-3, it is evident that when the sample temperature is raised to  $-78^{\circ}$ C. the outer peaks diminish and finally disappear, and the width of peak B decreases with the time of heating. Now, during radiolysis of PVC there are at least seven radicals which can be generated initially. These are:

- 68 -

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# FIGURE IV-4 ·×.

EFFECT OF TIME AT ROOM TEMPERATURE, ON THE SHAPE OF THE SIGNAL OBTAINED FROM A  $\gamma$  IRRADIATED SAMPLE OF PVC-A.

x. This figure shows the change in the signal shape, not the intensity.

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AT ZERO TIME AFTER IRRADIATION.

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SIGNAL RECORDED AT LIQUID NITROGEN TEMPERATURE.

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AFTER THREE HOURS AT ROOM TEMPERATURE. SIGNAL RECORDED AT LIQUID NITROGEN TEMPERATURE.

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# TABLE IV-3

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# Y-IRRADIATED PVC-A SAMPLE

Thermal History	No. of peaks	Width, in Gauss 1st peak	∆ Hmsl, 2nd peak	Intensity of signal in chart paper <u>divisions</u>	
		A	В	Peak A	В
At -78 <sup>0</sup> C. Time in hrs.					
0	2	50	50	57	72
15	2	49	42	48	62
30	2	49	39	47	61
49	2	48	38	40	52
At Room Temp.					
5 min.	2	47	36.5	30	51
3 hours	1		32		56

Dose:5 Mrads Irradiation Temp: -190<sup>0</sup>C

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The initial signal probably represents a mixture of some of these radicals. However, after heating, only the narrow signal B of g value  $2.0026\pm.0004$  remains. Ohnishi <u>et al</u><sup>(6)</sup> suggest this to be a polyene radical. On this basis, signal B could be associated with a mixture of following radicals:

-CHCl-(CH=CH)<sub>n</sub>-CH-CHCl-VIII

-CH-(CH=CH)<sub>n</sub>-CH<sub>2</sub>-CHCl-

In the same paper Ohnishi  $\underline{et al}^{(6)}$  showed that with the increase in the value of n (the length of the double bond sequence) the width of the signal decreased.

Since with the heat treatment of sample a narrow singlet of  $\Delta$  Hmsl of 12 G was obtained, it

- 71 -

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appears that the conjugation double bond length is very high. This type of radical would be expected to exhibit a high stability not being able to do an abstraction reaction and being unlikely to couple. In other words, radicals of this type would not decay at a fast rate.

The radical obtained by thermal degradation of Sample A, in the present study, was found to be very stable, indeed. When Sample A was heated in a nitrogen atmosphere and then sealed and left at room temperature, little change in spin concentration occurred. (Fig. IV-5).

It is therefore concluded that in the E.S.R. measurements made during the thermal degradation of PVC, we are looking at a polyene radical, in which the unpaired electron is delocalized, and is stabilized by bond resonance. It also appears to be safe, at this juncture, to conclude that the thermal dehydrochlorination of PVC is a radical process.

An attempt to gain further insight into the role of this particular radical was made by decomposing the polymer in the presence of a chain transfer agent, triphenylmethane, which had been shown to be a terminating agent in the decomposition of  $PVCl_2^{(10)}$ .

IV-5 EFFECT OF CHAIN TERMINATOR - TRIPHENYL METHANE

Burnett and Haldon<sup>(10)</sup>, used triphenyl methane

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RADICAL DECAY AT ROOM TEMPERATURE; SAMPLE PVC-A, HEATED IN N<sub>2</sub> ATMOSPHERE, AT 215<sup>°</sup>C.

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in studying the kinetics of the dehydrochlorination of Polyvinylidene chloride. They proposed that the hydrogen of triphenyl methane was abstracted by the macroradical, R., produced during the degradation of polyvinylidene chloride.

$$(C_6H_5)_3 \xrightarrow{CH} + R \xrightarrow{\cdot} \longrightarrow (C_6H_5)_3 \xrightarrow{C \cdot} + RH$$
 (IV-1)

The resonance stabilization of triphenylmethyl radical is such that it is not capable of abstracting from the macromolecule, and therefore, it cannot take part in the propagation step. The chain transfer reaction shown above, thus becomes a termination step.

Polymer sample A was mixed with triphenyl methane (.034 moles/100 g. PVC) in the presence of petroleum ether, which was later evaporated, and HCl evolution and spin generation on heating the sample in a  $N_2$ atmosphere were measured in the usual way. The results obtained are shown in Figures IV-6 and IV-7.

In the presence of  $(C_6H_5)$  C-H, the usual HCltime curve was broken into two portions having two different slopes. In Table IV-4, these slopes are termed as initial and final rates. The spin generation, however, proceeded at a very slow rate, and exhibited only one slope. Rates calculated from Fig. IV-6 are given in Table IV-4.

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EFFECT OF  $(C_{6}H_{5})$  CH ON THE THERMAL DEHYDROCHLORIN-ATION OF PVC. SAMPLE: PVC-A , ATMOSPHERE: NITROGEN (O) PURE PVC-A AT 238°C, ( $\Delta$ ) PVC-A +  $(C_{6}H_{5})$  CH AT 240°C.

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EFFECT OF  $(C_{6}H_{5})$  CH ON SPIN GENERATION. SAMPLE: PVC-A , ATMOSPHERE: NITROGEN (O) PURE PVC-A AT 238°C, ( $\Delta$ ) PVC-A +  $(C_{6}H_{5})$ CH AT 240°C.

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THERMAL DECOMPOSITION OF PVC-A IN NITROGEN ATMOSPHERE.					
Sample	Temp. <sup>O</sup> C.	wt. of (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> CH moles/100 g.	$\frac{dHCl}{dt} \times 10^{8}$ moles/g./sec.	$\frac{dSpin}{dt} \times 10^{12}$ moles/g./sec.	
рvс-а рvс-а+ (с <sub>6</sub> н <sub>5</sub> ) <sub>3</sub> сн	238 240	0 .034	447.00 ini- 39.0 tial fin-318.00 al	195.0 ini- 0.56 tial fin- 0.56 al	

TABLE IV-4

EFFECT OF  $(C_{6}H_{5})_{3}CH$  ON  $\frac{dHCl}{dt}$  AND  $\frac{dSpin}{dt}$  OBTAINED BY

(Since the curves for the sample containing triphenylmethane are broken into two portions, the rates referred to in Table IV-4 are calculated from the slopes of the linear portion of the curves, whereas, for the pure sample of PVC-A, these are calculated from the slopes at the time where 10% of the total theoretical decomposition had occurred. This treatment will be further discussed on page 87). From these data it is evident that the transfer agent,  $(C_{6}H_{5})_{3}$  CH, grossly retards the dehydrochlorination reaction, while at the same time reducing the number of spins. The loss in the spins probably being due to coupling of the diffusable  $(C_{6}H_{5})C$  radical with each other, or with some other radical. In other words, the propagating chains are terminated by reaction with  $(C_{6}H_{5})_{3}$  CH. It is therefore, concluded that the radicals are necessary to the decomposition of PVC and are not simply a by-product of the decomposition reaction. This observation lends further support to the thesis that the dehydrochlorination is a radical chain process.

At this juncture, we have established that the radical is necessary to the degradation of PVC, and have also established that the radical is a polyene resonance stabilized radical. We can now begin to determine a number of factors which should give us some insight into the overall reaction mechanism. Specifically, these are (1) the relationship between structural entities in the polymer, and the rate of radical generation (2) the energetics and the rate of radical generation, relative to those of HCl evolution, etc.

#### IV-6. SIMULTANEOUS MEASUREMENTS OF ELECTRON SPIN RESONANCE AND HC1 EVOLUTION

Simultaneous measurements of HCl evolution and

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spin generation were performed, by the method described in Chapter III, on all four samples PVC-A, PVC-B, PVC-C and PVC-D, at several temperatures. The results at 224<sup>o</sup>C. are shown in Figures IV-8, and IV-9. In Fig. IV-8, the amount of HCl evolved with the time of heating of the samples are plotted, while Fig. IV-9 shows the number of spins generated as a function of the time of heating.

In Figures IV-8 and IV-9, the HCl evolution and spin generation are seen to undergo a slow initial rise, followed by a rapid degradation, and then a levelling off where no further reaction is evident. (It is interesting to note that the spin concentration increases throughout the degradation, and then persists, thus the simple chain termination by coupling suggested by Stromberg, Straus & Achhammer<sup>(11)</sup> does not appear to be an acceptable thesis. This point will be further discussed in detail under "termination step").

These figures show that the homopolymers, PVC-A and PVC-B, are more stable than the samples containing propenyl chloride comonomer (PVC-C and PVC-D). The slopes for spin generation and HCl evolution are higher for both copolymer samples, PVC-C and PVC-D. In the case of PVC-C, the total HCl evolution at 224°C. is observed to be lower than the other samples. This may be associated with the high crystallinity of the sample.

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HC1 EVOLUTIONS WITH TIME AT 224<sup>O</sup>C. IN NITROGEN ATMOSPHERE.

(O) PVC-A, (X) PVC-B, ( $\Delta$ ) PVC-C, ( $\Box$ ) PVC-D.

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SPIN GENERATION WITH TIME AT 224<sup>O</sup>C. IN NITROGEN ATMOSPHERE.

(O) PVC-A, (X) PVC-B, ( $\Delta$ ) PVC-C, ( $\Box$ ) PVC-D.

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Of the linear samples, PVC-B has the lowest slopes for both spin generation and HCl evolution.

#### IV-7 ORDER OF REACTION

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The data for the thermal dehydrochlorination of PVC-A at different temperatures, from Table IV-5, have been replotted in Fig. IV-10 for the first order of reaction. In this figure, the abscissa represents the time of heating in minutes and ordinate represents  $\log \frac{a}{a-x}$ , where 'a' is the concentration of HCl in moles per g. of PVC present at zero time of heating and x is the moles of HCl evolved at time t. This figure shows that PVC dehydrochlorination in the range from about 5% to 50% of decomposition is a first order reaction, with respect to the monomer concentration; that is

$$\frac{dHCI}{dt} = K [C] \qquad (IV-2)$$
$$- \frac{d[C]}{dt} = K [C] \qquad (IV-3)$$

where K is the first order rate constant and C is the concentration of undecomposed monomer units in the polymer (which is equal to the amount of HCl present in PVC sample at time t). The first order rate constants for dehydrochlorination of samples PVC-A, PVC-B, PVC-C and PVC-D are given in Table IV-6, along with the activation energies derived from plots of log K vs. 1/T. (Fig. IV-11)

### TABLE IV-5

THE DATA FOR FIRST ORDER OF REACTION FOR HCL EVOLUTION

ΓA	215 <sup>0</sup> C	IA	224 <sup>0</sup> C	TA	233 <sup>0</sup> C.
Time, Min.	a/* a-x	Time, Min.	a∕ * a-x	Time, Min.	a∕ * a−x
0	1.00	0	1.00	о	1.00
60	1.07	45	1.08	20	1.025
70	1.13	55	1.18	28	1.10
80	1.20	65	1.33	33	1.20
90	1.30	75	1.46	35	1.25
100	1.40	80	1.52	43	1.45
110	1.50	85	1.59	55	1.80
120	1.60	. 90	1.67	63	1.90
130	1.70	101	1.80		
144	1.82	111	1.90		

FROM THE THERMAL DECOMPOSITION OF PVC-A.

(\* Where 'a' is the total concentration of HCl in moles per gram of PVC present at zero time and 'x' is the amount of HCl evolved at time 't'.) і 83

FIRST ORDER PLOT FOR HCL EVOLUTION BY THE THERMAL DEGRADATION OF PVC SAMPLE A. (O) AT 233<sup>O</sup>C. , ( $\Delta$ ) AT 224<sup>O</sup>C. , ( $\Box$ ) AT 215<sup>O</sup>C.

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ACTIVATION ENERGY PLOT FOR HC1 EVOLUTION, USING FIRST ORDER RATE CONSTANT, K.

REACTION ATMOSPHERE : NITROGEN.

(0)	PVC-A,	TEMPERATURE	RANGE	:	215 - 233°C.
(X)	PVC-B,	TEMPERATURE	RANGE	:	215 - 243 <sup>0</sup> C.
(∆)	PVC-C,	TEMPERATURE	RANGE	:	188.5-224 <sup>0</sup> C.
(_)	PVC-D,	TEMPERATURE	RANGE	:	188.5-224 <sup>o</sup> C.

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In the present work, activation energies are calculated by the least square method using a computer programme.

A four-fold difference in activation energies is apparent with the highest value being associated with the linear sample PVC-B, and the lowest with the sample containing the tertiary chlorine species.

#### TABLE IV-6

FIRST ORDER RATE CONSTANTS FOR DEHYDROCHLORINATION

Sample	Temp. <sup>O</sup> C.	(a) K x 10 <sup>5</sup> sec <sup>-1</sup>	(b) E'HCl Kcal/mole
PVC-A	215 224 233	11.5 15.6 25.7	22 ± 2
PVC-B	215 224 233 243	2.5 4.7 35.2 54.0	52 ± 10
PVC-C	188.5 206 224	5.8 38.3 52.5	28 ± 5
PVC-D	188.5 206.0 215 224	15.3 20.3 29.0 34.5	11 ± 1

OF PVC SAMPLES.

- (a) K is the first order of reaction rate constant for HCl evolution.
- (b)  $E'_{HCl}$  is the activation energies for HCl evolution, derived from the plots of log K vs.  $\frac{1}{T}$  (Figure IV-11)

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The concentration of spins at any time, is going to be a function of the concentration of initiating sites and the chain transfer, etc., and hence it is impossible to define a rate constant for spin generation. However, a comparison of the rates can be used in order to determine the relationship with the rate of HCl evolution and the reaction energetics. For this purpose, the rates at some particular point of decomposition can be taken. We have arbitrarily chosen to make the comparison at the point, where 10% of the theoretical HCl evolution had occurred in each sample. These comparative data are shown in Table IV-7. In this Table, the rates for both HCl evolution and spin generation are calculated from the slopes at the times where 10% of the theoretical HC1 had evolved.

The values of Table IV-7 are calculated from Figures IV-8 and IV-9, and from Figures AIII-1 to AIII-8, in the Appendix. This table reveals the fact that with the rise in temperature,  $\frac{dHC1}{dt}$ ,  $\frac{dSpin}{dt}$  both increase, but the apparent chain length for HCl evolution, defined as  $\frac{dHC1}{dt}$ ,  $\frac{dSpin}{dt}$ , decreases. This suggests that HCl evolution and spin generation both have positive activation energies, while the chain lengths have negative values.

Having determined the order of reaction, it is instructive to calculate the activation energies for HCl

- 87 -

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### TABLE IV-7

# RATES OF DEGRADATION AT VARIOUS TEMPERATURES, OF POLYVINYL-

Sample	Temperature <sup>O</sup> C.	$\frac{dHCl}{dt} \times 10^{8*}$ moles/g./sec.	<pre>dSpin x 10<sup>12*</sup> moles/g./sec.</pre>	Chain length (v) x $10^{-4}$ (= $\frac{dHC1/dt}{dSpin/dt}$ )
PVC-A PVC-B PVC-C PVC-D	215 224 233 215 224 233 243 188.5 206 224 188.5 206 215	130.5 197.9 338.8 30.7 57.9 335.7 772.2 95.2 458.3 916.6 215.2 262.8 392.8	$   \begin{array}{c}     10.5 \\     25.1 \\     94.0 \\     1.7 \\     4.3 \\     39.2 \\     442.7 \\     1.4 \\     13.0 \\     233.2 \\     11.7 \\     54.4 \\     89.9 \\     210.2 \\   \end{array} $	$     \begin{array}{r}       12.3 \\       7.8 \\       3.6 \\       17.6 \\       13.4 \\       8.5 \\       1.7 \\       65.6 \\       35.2 \\       3.9 \\       18.3 \\       4.8 \\       4.3 \\       2.2 \\     \end{array} $

## CHLORIDE SAMPLES

\* Rates measured from slopes at time where 10% of total theoretical decomposition had occurred.

н 88 - evolution and spin generation, for all four samples. For the activation energy of HCl evolution, either the calculated first order rate constants can be used (Table IV-6), or the slopes of the HCl vs. time curve at 10% theoretical decomposition can be utilized. However, the temperature coefficient of spin generations, since we are not able to determine a formal rate constant, are calculated only from the slopes of spin-time curve.

#### IV-8 ACTIVATION ENERGIES

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The rates from Table IV-7, were used to calculate the activation energies for spin generation and HCl evolution. These activation energies are given in Table IV-8, along with the activation energies for HCl evolution, determined by the plot of log K vs. l/T(from Table IV-6).

In the calculation of energies, the least square method was applied by means of a computer programme.

The utilization of the 10% slope in making our comparison would appear to be justified, on the basis of comparison of first and second columns in the following Table. The activation energies for the HCl evolution for the "commercial sample", PVC-A, are within the general range that has been observed for the majority of the PVC samples (Table IV-9).

#### TABLE IV-8

Sample	(a)	,(b)	(c)
	<sup>E</sup> HCl	<sup>E</sup> HCl	E Spin
	Kcal/mole	Kcal/mole	Kcal/mole
PVC-A	26 ± 1	22 ± 2	56 ± 3
PVC-B	61 ± 5	52 ± 10	107 ± 8
PVC-C	29 ± 3	28 ± 5	61 ± 3
PVC-D	16 ± 4	11 ± 1	34 ± 1

ACTIVATION ENERGIES FOR THE DEHYDROHALOGENATION OF POLY-VINYL CHLORIDE SAMPLES

- (a) <sup>E</sup>HCl : Activation energies for HCl evolution calculated by using the rates of HCl evolution at the time where 10% of the theoretical HCl evolved. (Fig. IV-12).
- (b) <sup>E</sup>HCl : Activation energies for HCl evolution,
   derived from the plots of log K vs. 1/T. (Fig. IV-11).
- (c) E Spin: Activation energies for spin generation derived by using the rates of spin generation at the same degree of degradation (10% of the theoretical HCl evolved) (Fig. IV-13).

ACTIVATION ENERGY PLOT FOR HC1 EVOLUTION USING  $\frac{dHC1}{dt}$  AS A RATE.

REACTION ATMOSPHERE - NITROGEN.

(0)	PVC-A,	TEMPERATURE	RANGE	:	215 - 233°C.
(X)	PVC-B,	TEMPERATURE	RANGE	:	215 - 243 <sup>0</sup> C.
(∆)	PVC-C,	TEMPERATURE	RANGE	:	188.5-224 <sup>0</sup> C.
(_)	PVC-D,	TEMPERATURE	RANGE	:	188.5-224 <sup>0</sup> C.

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ACTIVATION ENERGY PLOT FOR SPIN GENERATION USING  $\frac{dSpin}{dt}$  AS A RATE. REACTION ATMOSPHERE - NITROGEN.

(0)	PVC-A,	TEMPERATORE	RANGE	ě	215 -	255 C.
(X)	PVC-B,	TEMPERATURE	RANGE	:	215 -	243 <sup>0</sup> C.
(∆)	PVC-C,	TEMPERATURE	RANGE	:	188.5-	-224 <sup>0</sup> C.
(0)	) PVC-D,	TEMPERATURE	RANGE	:	188.5-	-224 <sup>0</sup> C.

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TABLE	IV	-9
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Sample	Temp. Range <sup>O</sup> C.	<sup>E</sup> HCl Kcal/mole	Ref.	
PVC (ICI)	208 - 223	28 <sup>.</sup>	Graisse	12
PVC (-)		29	Hartmann	13
PVC Geon 101		34	Arlman	14
PVC (AZO)	235 - 260	26	Stromberg et al	11
PVC (bp)	18	32	11	
PVC (γ-rays)	235 - 250	30	N ,	
PVC (Sicron	200 - 250	33(in 1	N <sub>2</sub> )Talamini	15
(Suspa) "	11	24(in (	0 <sub>2</sub> ) "	U
PVC (AIBN)	178 - 212	22.8-2	4 Bengough & Sharpe	16
PVC (-)	193 - 233	28	Crosato	17

#### ACTIVATION ENERGIES FOR DEHYDROCHLORINATION OF PVC

# IV-9 CORRELATION OF SPIN GENERATION AND THE INITIATION STEP

The role of the radical in the degradation of PVC is obviously of complex nature. From the data presented thus far, it is evident that the overall decomposition is integrally tied to the presence of the radicals. However, the rate of HCl evolution is not a simple function

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of spin concentration. Were it directly proportional, the HCl rate would be expected to reach explosive proportions at the high concentrations of radicals present at advanced stages of decomposition. Since the observed rates for HCl evolution do not follow this behaviour, it is concluded that there is a steady state concentration of <u>active radicals</u> present at any time, with their specific <u>concentration being related to the rate of increase of spins</u>, <u>but not to the total concentration</u>. The total concentration includes those propagating, as well as those which are dormant through either exhaustion of HCl in their chains, or through their being positioned at a point which will not allow a new propagation step.

In summary, the radicals are not simply a product of the dehydrochlorination process. Rather, they exhibit another rate and another activation energy. An important correlation, which we have previously noted, is that the activation energies for spin generation parallel the activation energies for the decomposition of model compounds in the gas phase (Table IV-2 and IV-8). This suggests that the rate of spin generation is associated with the rate of initiation of the dehydrochlorination process. We thus propose that the activation energies for the spin generation are those for carbon-chlorine bond dissociation, with the latter being the initiation step.

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IV-10 REACTION MECHANISM

On the basis of the above arguments, we have now established the energetics for what we consider to be the initiation (E Spin) and the overall <u>reactions</u> (E HCl)

In choosing a mechanism, the following factors must be considered:

- 1) The dehydrochlorination is a radical reaction : Sections IV-3, and IV-4.
- 2) It is a radical chain process : Section IV-5.
- 3) The dehydrohalogenation is first order with respect to the chlorine content of the polymer or monomer unit: Section IV-7.
- 4) The activation energy for the decomposition changes with changes in the polymer structure.
   Table IV-8.
- 5) The decomposition is accompanied by a growth in resonance stabilized radicals. The activation energies associated with their production , parallel the values for the gas phase decomposition of chlorine containing model compounds. - Tables IV-2 and IV-8.

Using the above considerations, a radical chain

mechanism, having initiation, propagation and termination steps, is proposed. In the following section, a discussion of these steps for a linear PVC and each of the copolymers is undertaken.

#### Initiation

Step

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$$(1) -CH_2 - CHCl - CH_2 - CHCl - \xrightarrow{k_1} - CH_2 - CH - CH_2 - CHCl + Cl \cdot (R_1 \cdot) (IV-4)$$

$$(2) R_1 \cdot + - CH_2 - CHCl - CH_2 - CHCl - \xrightarrow{k_2} R_1 - H + - CH - CHCl - CH_2 - CHCl - (R_2))$$

$$(1V-5)$$

(3) 
$$Cl \cdot + -CH_2 - CHCl - CH_2 - CHCl - \xrightarrow{k_3} - CH - CHCl - CH_2 - CHCl - + HCl$$
  
(R<sub>2</sub>·)  
(IV-6)

(4) 
$$-CH-CHCl-CH_2-CHCl- \xrightarrow{k_4} -CH=CH-CH_2-CHCl-+Cl$$
  
(R2) (IV-7)

(5) 
$$Cl \cdot + R_2 \cdot \xrightarrow{k_5} R_2 Cl$$
 (IV-8)  
(6)  $Cl \cdot + -CH_2 - CHCl - CH_2 - \xrightarrow{k_6} HCl + -CH_2 - CCl - CH_2 - (R'_1 \cdot) (IV-9)$ 

# IV-11 RATIONALIZATION OF PROPOSED REACTION SCHEME

IV-11-1 Initiation

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The high activation energies for spin generation suggest that initiation is a simple thermally induced bond (3) rupture process, of the kind proposed for the model compounds. Their correlation with the activation energies for the decomposition of model compounds was noted in Section IV-9.

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That the ruptured bond should be a C-Cl bond, is suggested by Table IV-10.

#### TABLE IV-10

BOND DISSOCIATION ENERGIES IN SOME MODEL COMPOUNDS OF PVC<sup>(18)</sup>

Compound	ot c	QC-Cl Kcal/mole	Q <sub>C-H</sub> Kcal/mole
2,4-dichloropentane	347-397	74.2	94.8
2,4,6-trichloroheptane	346-386	74.0	94.6
3-ethyl-3-chloropentane	230-270	70.9	91.7
2-methyl-2-chlorobutane		72.8	92.3
4-chloro-2-pentene	297-345	56.5	95.3
6-chloro-2,4-hepta-diene	302-347	56.0	95.3

These data show that the C-Cl bond is the weakest one in the alkyl chloro- compounds and in turn, that there are variations in the bond strength with the structure. Thus, in the thermally induced initiation step, the cleavage of C-Cl bond can be expected to take place.

The energetics for d Spin/dt are thus concluded to pertain to Step 1 (Reaction IV-4).

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#### IV-11-2 Propagation

Among the propagation steps which have been proposed, is the abstraction of hydrogen atom by a chlorine radical. There are two possibilities for such a reaction.

$$cl. +-CH_2-CHCl-CH_2-CHCl- \rightarrow -CH-CHCl-CH_2-CHCl-+HCl$$

$$(IV-6)$$

$$cl. +-CH_2-CHCl-CH_2-CHCl- \rightarrow -CH_2-CCl-CH_2-CHCl-+ HCl$$

$$(IV-9)$$

Between these two possible reactions, the literature would indicate that reaction (IV-6) is preferred on the basis of energetics. Fuchs and Louis <sup>(19)</sup> showed, through PVC chlorination, that hydrogens of the  $CH_2$  group disappeared, rather than those associated with the chloromethylenic group. This is in keeping with the abstraction energetics for the various C-H bonds. Thus, by abstraction of a hydrogen atom, a  $\beta$  chlororadical is obtained by (IV-6). Now, let us see what the possible reactions are for this kind of radical.

Barton<sup>(20)</sup> discussed the pyrolysis of alkyl chlorides. According to him, the reaction mechanism is strongly dependent on the position of the various groups in the radicals. If the rearrangement of a reaction intermediate yields a chain carrier, then the reaction will be a radical chain otherwise, unimolecular. He showed that the reaction intermediate of structure [X] can rearrange

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itself to give a double bond and Cl. .

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$$CH_{2}Cl-CHCl \longrightarrow CH_{2}=CHCl + Cl. (IV-10)$$

$$[X]$$

$$CH_{3}-CCl_{2} \longrightarrow CH_{2}=CHCl + Cl. (IV-11)$$

$$[Y]$$

Therefore, the decomposition of alkyl chlorides, in which the reaction intermediate of structure [X] which yields a Cl· is obtained, will be by a radical chain mechanism. However, if the reaction intermediate of structure [Y] is obtained, for which the rearrangement is not possible, the reaction will proceed via a non-chain mechanism.

Since the PVC dehydrochlorination is shown in the present study to be a radical chain process, then according to Barton's hypothesis, it should have a reaction intermediate of structure -CH<sub>2</sub>-CHCl-CH-CHCl-, which will rearrange itself to yield a double bond and a chain carrier Cl. atom.

$$-CH_2$$
-CHCl-CH-CHCl-CH<sub>2</sub>-CHCl- (IV-7)

-CH<sub>2</sub>-CHCl-CH=CH-CH<sub>2</sub>-CHCl-+Cl·

Hence, the propagation step in PVC dehydrochlorination is made up of two reactions:

(i) Abstraction of methylenic hydrogen by Cl.
$$Cl \cdot + -CH_2 - CHCl - CH_2 - CHCl - - CH - CHCl - CH_2 - CHCl - + HCl$$
  
(R<sub>2</sub> ·) (IV-6)

Reactions (i) and (ii) are Steps 3 and 4, respectively, in the proposed kinetic scheme.

The abstraction of hydrogen by reaction (IV-6) (Step 3), is a low energy process, requiring between 1 and 5 Kcal/mole<sup>(22)</sup>, depending upon the nature of the C-H bond being broken.

The order of reactivity of C-H bonds to radical abstraction is as follows: tertiary > secondary > primary. Barton and Howlett<sup>(21)</sup> showed that reaction (IV-7) (step 4), which involves the expulsion of Cl· by the reaction intermediate, has an activation energy of 20-22 Kcal/mole.

IV-11-3 Termination

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In discussing the termination process involved in a chain reaction, one has to discuss it in terms of the destruction of one of the various reactive species. In this context, the following are the steps which can result in the termination of the chain:  $Cl \cdot + Cl \cdot \longrightarrow Cl_2$  (IV-12)

Cl• +	$R_1 \cdot \longrightarrow R_1 C_1$	L		(IV-13)
R <sub>1</sub> ∙ +	$R_2 \cdot \longrightarrow Cros$	sslinked	product	(IV-14)
R <sub>2</sub> • +	R <sub>2</sub> · →	11	11	(IV-15)
$R_{1} \cdot +$	$R_1 \cdot \longrightarrow$	11	11	(IV-16)

Previous authors have discussed some of these combinations. Stromberg et al <sup>(11)</sup> accepted only reaction (IV-12), as being the termination of the chain, but their solution to the kinetic analysis yielded a 1.5 order, with respect to the concentration of monomer units in the polymer. This is not the order which we observe. Furthermore, their proposal neglects two experimental facts, (1) that there is no measurable chlorine in the gaseous products, and (2) that there are radicals found in the final reaction product. The fact <sup>(11,12)</sup> that they found a 1.5 order could be associated with the complex chemistry which is going on at the very high temperatures they utilized in their study. Bengough and Sharpe<sup>(16)</sup> however, agree with the present work in the first order kinetics.

Let us consider each of these possible termination steps:

In the present work, the retention of the high spin concentration at the end of the HCl evolution suggests that chain termination by coupling is not the only termina-

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tion step. While such a reaction may occur, the persistance of high concentrations of radicals leads us to believe that termination must also result from the trapping of radicals. This trapping can be a process where a radical on the polymer chain ends up at some structural point which does not allow a continued propagation. Winkler<sup>(23)</sup> would be in a measure of agreement with this proposal. According to him, the abstraction of a hydrogen atom from -CHCl-by Cl<sup>.</sup>, leaves behind a macroradical which cannot rearrange to give another Cl<sup>.</sup>, but can abstract a secondary hydrogen atom from another chain.

Thus, the termination step could be any of the following types:

 The simple coupling reactions of the radicals, as shown in reactions (IV-8) and (IV-12) to (IV-16).

2) The abstraction of hydrogen from -CHClto leave an inactive macroradical, which cannot propagate the chains.

Since the dehydrochlorination is a radical chain reaction, let us consider only those steps which involve the chain carrier Cl<sup>.</sup>. Since chlorine has not been found in the gaseous product of pyrolysis by previous workers<sup>(24)</sup>

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nor in the present study, the termination by coupling of two chlorine radicals, reaction (IV-12), is rejected as an important termination reaction. Furthermore, although reaction (IV-14) to (IV-16) can be present in a condensed phase, the diffusion of macroradicals is very slow, and thus these steps are not considered likely as candidates for the rate determining termination steps. They are therefore, neglected. On this basis, we are left with Steps (5) and (6) of the kinetic scheme.

Step 5.

$$Cl \cdot + R_2 \cdot \xrightarrow{K_5} R_2 Cl$$
 (IV-8)

#### Step 6.

$$cl + -ch_2 - chcl - ch_2 - chcl - \xrightarrow{k_6} - ch_2 - \dot{c}clch_2 - chcl + hcl$$
  
(IV-9)

Let us now see how these reactions interrelate to the initiation and propagation steps.

An obvious termination is Step 5, involving the two species from the propagation steps, a  $Cl \cdot R_2 \cdot coupling$ . However, if  $k_2$  (reaction IV-5) is very small compared to  $k_3$ , (reaction IV-6), then Step 6 is also a virtual termination step. Now, since Step 2 involves the diffusion of a macroradical, which will abstract hydrogen less efficiently than the Cl<sup>.</sup>, it is reasonable to assume that  $k_2$  is

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None of the proposed termination reactions requires a large energy of activation to effect bond coupling or abstraction. However, there is the possibility that the process shown in reactions (IV-8) and (IV-9) are diffusion controlled, and as such, could require activation energies in excess of 25 Kcals/mole <sup>(25)</sup>.

Having rationalized the initiation, propagation and termination steps, which we have proposed, let us solve for the order of reaction and the energetic relationship which must follow.

#### IV-12. THE KINETIC SOLUTION FOR HC1 EVOLUTION

Applying the 'steady state' condition for radicals  $Cl \cdot$ ,  $R_1 \cdot$  and  $R_2 \cdot$  to the proposed reaction scheme, the following solution is obtained:

 $(2k_{3}k_{5}+k_{5}k_{6})$   $[C1]^{2} + k_{4}k_{6}$   $[C1] - 2k_{1}k_{4} = 0$  (IV-17)

(The calculations for the above solution (IV-17) are given in Appendix AII-1.)

On the basis of the previous discussion regarding Step 6, and in consideration of the high activation energy for Step 4, relative to Step 3, the product of  $k_4k_6$  must be a very small number. Similarly,  $k_5k_6$  will be much smaller than  $k_3k_5$ . It is therefore, possible to

re-write Equation (IV-17) as

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$$2k_{3}k_{5}[Cl\cdot]^{2} = 2k_{1}k_{4}$$
 (IV-18)

and

$$[C1^{-}] = \left[\frac{k_1 k_4}{k_3 k_5}\right]^{\frac{1}{2}}$$
 (IV-19)

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From the reaction scheme, it is apparent that

$$\frac{d[HC1]}{dt} = k_3[C1 \cdot ][C] + k_6[C1 \cdot ][C]$$
(IV-20)

Substituting [Cl·]from Equation (IV-19) into (IV-20) and neglecting  $k_4^k_6$ , once again, yields

$$\frac{d[HC1]}{dt} = \left(\frac{k_1 k_3 k_4}{k_5}\right)^{\frac{1}{2}} [C]$$
 (IV-21)

and the overall rate can be expressed as

$$\frac{d[HC1]}{dt} = k_0 [C] \qquad (IV-22)$$

where

$$k_{0} = \left(\frac{k_{1}k_{3}k_{4}}{k_{5}}\right)^{\frac{1}{2}}$$
 (IV-23)

This solution exhibits the first order dependence, which is required by the experimental observations. The proposed reaction scheme is thus, to this point, a rational one.

The total scheme can now be tested by solving for the activation energies associated with the various rate constants.

# IV-13 VERIFICATION OF MECHANISM BY ENERGETICS

From the Arrhenius relation, log k =  $-\frac{E}{RT}$  + Constant, the activation energy dependence of Equation (IV-23) can be written as

$$E_{0} = \frac{1}{2}(E_{1} + E_{3} + E_{4} - E_{5}) \qquad (IV-24)$$

where  $E_0$  is the overall activation energy for HCl evolution, and  $E_1$ ,  $E_3$ ,  $E_4$ , and  $E_5$  are the activation energies for Steps 1, 3, 4 and 5, respectively.

Let us first consider these quantities for PVC-A, the commercial sample for which we found an  $E_{spin}$ which we equate to E (initiation) or  $E_1$ , of 56 Kcals/mole. The overall activation energy for HCl evolution in this sample,  $E_0$ , was 26 Kcals/mole. Thus, by assigning an  $E_4$  of 21 Kcals/mole to Step 4, as required by the Barton-Howlett experiment<sup>(21)</sup>, and 4 Kcals/mole for the abstraction, Step 3<sup>(22)</sup>, we can solve for the activation energy for termination,  $E_5$ .

> $26 = \frac{1}{2}(56 + 4 + 21 - E_5)$  (IV-25)  $E_5 = 81 - 52 = 29 \text{ Kcals/mole (IV-26)}$

This activation energy for the termination is a relatively high value, and is thought to be due to the diffusion of the chlorine radical in the condensed phase. On the basis of recent studies for krypton, where the activation energy for diffusion in PVC films above their  $T_g$  was found to be 30 Kcals/mole<sup>(25)</sup>, the 29 Kcals/mole value for the

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diffusion of chlorine is considered to be quite reasonable.

Furthermore, it is reasonable to conclude that  $E_5$ , if it is indeed related to the energy of diffusion, will be the same in all samples. The  $E_0$ 's for PVC-B, PVC-C and PVC-D, can now be calculated, using the measured initiation energetics, and the results compared to the experimental values. Table IV-11 shows these results, and it is obvious that a remarkable correlation between structure and activation energy exists.

#### TABLE IV-11

CALCULATION OF OVERALL ACTIVATION ENERGY E

Sample	E <sub>1</sub> + E <sub>3</sub> + E <sub>4</sub> - E <sub>5</sub> = E <sub>0</sub> (Calculated) Kcal/mole	E <sub>o</sub> (Found) Kcal/mole
PVC-B PVC-C PVC-D	$\frac{1}{2}(107 + 4 + 21 - 29) = 51.5$ $\frac{1}{2}(61 + 4 + 21 - 29) = 28.5$ $\frac{1}{2}(34 + 4 + 21 - 29) = 15.0$	61 ± 5 29 ± 3 16 ± 4

Under circumstances where the observed values for  $E_0$  were closer than in the present case, the agreement found between calculated and experimental values would be considered interesting. Here, however, where we deal with values of  $E_0$ , ranging from 16 to 61 Kcals/mole, the agreement is considered to offer strong support for the proposed scheme. Further support derives from the broad range of  $E_{o}$ 

observed which, if associated with the initiating C-Cl bond cleavage, as proposed here, follow the exact order and nearly the precise energetics which model compound studies predicted.<sup>(3)</sup>

We therefore conclude this scheme to be most reasonable, and the best supported by experiment, to-date. The roles of the various structures in bringing about the observed energetics and rates can be rationalized as follows.

## IV-14. RATIONALIZATION OF THE EFFECTS OF STRUCTURAL IRREGULARITIES

#### IV-14-1. PVC-A

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This polymer has a linear structure with a branch every 400 monomer units<sup>(26)</sup>. These branches may be in the form of tertiary hydrogen or tertiary chlorine, or both. These are formed during the polymerization by the following processes:

 $R \cdot + -CH_{2} - CHCl - CH_{2} - CHCl - CH_{2} - CHCl - CHCl - (IV - 27)$   $-CH_{2} - CHCl - \dot{C}H - CHCl - + CH_{2} = CHCl - CH_{2} - CHCl - \dot{C} - CHCl - (IV - 28)$   $CH_{2} - CHCl - CH_{2} - CHCl - CH_{2} - CHCl - CH_{2} - CHCl - CH_{2} - CHCl - (IV - 28)$   $R \cdot + -CH_{2} - CHCl - CH_{2} - CHCl - CH_{2} - CHCl - CH_{2} - CHCl - (IV - 28)$   $-CH_{2} - \dot{C}Cl - CH_{2} - CHCl - CH_{2} - CHCl - CH_{2} - CHCl - (IV - 28)$   $CH_{2} - \dot{C}Cl - CH_{2} - CHCl - CH_{2} - CHCl - (IV - 28)$   $-CH_{2} - \dot{C}Cl - CH_{2} - CHCl - CH_{2} - CHCl - (IV - 28)$   $CH_{2} - \dot{C}Cl - CH_{2} - CHCl - CH_{2} - CHCl - (IV - 28)$   $CH_{2} - \dot{C}CH_{2} - CHCl - CH_{2} - CHCl - (IV - 28)$   $CH_{2} - \dot{C}CH_{2} - CHCl - CH_{2} - CHCl - (IV - 28)$   $CH_{2} - \dot{C}CH_{2} - CHCl - (IV - 28)$   $CH_{2} - \dot{C}CH_{2} - CHCl - (IV - 28)$   $CH_{2} - \dot{C}CH_{2} - CHCl - (IV - 28)$   $CH_{2} - \dot{C}CH_{2} - CHCl - (IV - 28)$   $CH_{2} - \dot{C}CH_{2} - CHCl - (IV - 28)$   $CH_{2} - \dot{C}CH_{2} - CHCl - (IV - 30)$   $CH_{2} - \dot{C}CH_{2} - CHCl - (IV - 30)$ 

(Tertiary Chlorine)

Since the abstraction of a methylenic hydrogen atom (reaction IV-27) by R· radical is easier than the abstraction of a chloromethylenic hydrogen atom (reaction IV-29), the formation of a tertiary hydrogen is more probable. Thus, PVC Sample A would be expected to have a larger number of tertiary hydrogens via reactions (IV-27) and (IV-28) than tertiary chlorines. The energetics of the initiation should be reflected in the model compound work on species containing a secondary chlorine atom. The agreement between  $E_{spin}$  in the polymer and the measured E for model compounds <sup>(3)</sup>, are concluded to reflect an initiation inyolving a secondary C-Cl bond cleavage.

IV-14-2 PVC-B

This linear polymer exhibits an exceedingly large  $E_{spin}$  despite the fact that it contains the same C-Cl bonds as PVC-A. The rise from 56 ± 3 to 107 ± 8 Kcal/mole in  $E_{spin}$  is thought to be associated with the melting behaviour of this highly linear polymer, rather than simply being a reflection of bond rupture. (The melting point of crystalline PVC has recently been found to cover the range of 150 to 300°C. depending on polymerization temperature<sup>(27)</sup>.

IV-14-3 PVC-C

This polymer, containing nine mole per cent of

1-chloropropene, has a large concentration of  $3^{\circ}$  hydrogen atoms, but retains the same  $2^{\circ}$  chlorine atoms as PVC-A. Therefore, the initiation energetics should be the same as for PVC-A, if the C-Cl cleavage is indeed the initial step. The coincidence of E  $_{\rm spin}$ , 56 ± 3, for PVC-A and 61 ± 3 for PVC-C, suggests this rationale to be correct. Since we are assuming the same propagation and termination for all cases, the overall activation should also be equal to that observed for PVC-A. This is in fact, what is observed for this polymer.

What then accounts for the much faster overall rate of decomposition of this polymer, as compared to PVC-A? We suggest the explanation lies with the presence of the tertiary hydrogen function and occurs because of the easier abstraction of that function, relative to a secondary hydrogen. The result being an increase in the steady state concentration of propagating radicals.

Referring to the overall mechanism, it is evident that there are two possible routes for a Cl. abstraction reaction. They are Step 3, which results in a continuation of the chain reaction, and Step 6, the abstraction of a hydrogen atom from a CHCl group, which results in a virtual termination. The fact that the dehydrohalogenation reaction proceeds so readily suggests  $K_3 >> k_6$ , with the difference being a reflection of the lower bond

energy of the methylene hydrogen <sup>(28)</sup> compared to the CHCl hydrogen. On this basis, the substitution of a tertiary hydrogen for the  $CH_2$  hydrogen should further emphasize the difference between  $k_3$  and  $k_6$ . This will result in a higher concentration of  $R_2$  and consequently, an accelerated decomposition.

IV-14-4. PVC-D

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This polymer containing six mole per cent of 2-chloropropene has a high concentration of easily ruptured tertiary carbon chlorine bonds (18), and therefore, it should undergo initiation more readily than the other three polymers. The reduction in  $E_{spin}$  to 34 Kcals/mole, close to the same reduction observed for model compounds  $^{(3)}$ , supports this thesis. Assuming once again, that the reaction paths are equivalent, following initiation, any reduction spin' (initiation), should result in a reduction in in Е the activation energy for HCl evolution. Table IV-8 shows that this is indeed the case. Thus, a reduction in is followed by predictable drop in E<sub>HCl</sub> The E. spin enhanced overall rate constant is then concluded to be associated with a large  $k_1$  in the reaction scheme.

IV-14-5 Structural Irregularities and Chain Lengths

Let us now see how this discussion tests kinetic chain lengths of decomposition process. The ratio of

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dHCl to d Spin over the linear portion of the curve yields dHCl of Spin which, when considered in the usual steady state manner, is a measure of relative kinetic chain lengths. Table IV-7, illustrates these data. The data, at 224°C, from this Table are presented in the form of ratios in Table IV-12, for the purpose of comparison.

#### TABLE IV-12

Polymer Sample	A	В	С	D
Structure: -	Regular	Linear	Tertiary H	Tertiary Cl
d HCl/dt x 10	4 1 0 <sup>8</sup> 1	0.29	4.6 9.3	2.3 8.4
$v = \frac{d HCl}{d Spin}$	1	1.7	0.49	0.28

COMPARISON OF RATES AND KINETIC CHAIN LENGTHS AT 224° C.

From this Table, several firm conclusions can be drawn.

1) Polymer sample PVC-B, which is a linear sample has a large value of kinetic chain lengths, which shows that the linear polymers do not initiate chains easily, but having been initiated, they have exceedingly long chain lengths for their decomposition.

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PVC-B > PVC-A > PVC-C > PVC-D

The above trend of kinetic chain lengths shows that with the inclusion of irregularities, chain lengths are lowered and that sample PVC-C, which contains tertiary hydrogen, has kinetic chain length greater than PVC-D having tertiary chlorine. Let us test this observation in these branched samples, in terms of rate constants and our previous discussion for the reaction mechanism of these samples.

The kinetic chain length from our reaction scheme will be given by

$$v \quad (\text{Kinetic chain length}) = \frac{\text{Rate of propagation (Rp)}}{\text{Rate of termination (Rt)}}$$
  
or 
$$v = \frac{k_3[\text{Cl}\cdot][\text{C}]}{k_5[\text{Cl}\cdot][\text{R}_2\cdot]+k_6[\text{Cl}\cdot][\text{C}]} = \frac{k_3[\text{C}]}{k_5[\text{R}_2\cdot]+k_6[\text{C}]}$$
  
(IV-31)

In Section Appendix AII-2, it is shown that  $R_2^{\bullet}$  could be expressed in the following manner:

$$[R_{2}^{\cdot}] = \left[\frac{2k_{1}k_{3} + k_{1}k_{6}}{2k_{4}k_{5}}\right]^{\frac{1}{2}} [C] \quad (IV-32)$$

Substituting this expression in (IV-31) and neglecting the term  $k_4 k_6$ , as we have done before, we obtain

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$$v = \left[\frac{k_{3}k_{4}}{k_{1}k_{5}\left(1 + \frac{k_{6}}{2k_{3}}\right)}\right]^{\frac{1}{2}}$$
 (IV-33)

From this solution, it is evident why the kinetic chain length for PVC-C is greater than for PVC-D. For PVC-C we have already mentioned that  $k_3 >> k_6$ . This relationship will reduce the second term in the denominator, making the kinetic chain length ( $\nu$ ) larger. Furthermore, in PVC-D, the  $k_1$  is higher than that for PVC-C. Thus, both factors will tend to yield a higher chain length for the tertiary hydrogen containing polymer.

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### SUMMARY AND CONCLUSIONS

A technique of simultaneous measurements of HCl evolution and spin generation during thermal degradation has been utilized to study the decomposition of polyvinylchloride. The results lead to the following conclusions.

- (i) The thermal degradation of PVC is a radical chain process for which the rate and activation energy for spin generation is associated with the initiation step.
- The postulated mechanism of the thermal (ii) degradation is based upon a three-step reaction scheme, involving initiation, propagation, and termination. The initiation step consists of the cleavage of a C-Cl bond. The Cl·radical produced in this step abstracts a hydrogen to generate an "active" radical which takes part in a two-step propagation reaction. The chain is terminated either by the coupling of two radicals, or by the abstraction of chloromethylenic hydro-The calculation of the activation energy gen. for the termination step (29 Kcal/mole) suggests that the termination step is diffusion controlled. The kinetic solution obtained from the proposed

mechanism reveals that the dehydrochlorination should be a first-order reaction, which is what was found experimentally.

(iii) The structural irregularities, tertiary hydrogen and tertiary chlorine atoms present in the polymer chain increase the rates of HCl evolution and spin generation. Tertiary hydrogen has no effect on the overall activation energy,  $E_{HCl}$ and on the activation energy for spin generation,  $E_{spin}$ , whereas, tertiary chlorine atoms reduce  $E_{HCl}$  and  $E_{spin}$ .

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#### REFERENCES

	1.	C.D.	Dovle,	Anal.	Chem.	33,	77	(1961)
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- J. Pellon, paper presented at the International Symposium on Inorganic Polymers, Nottingham, 1961.
- 3. M. Asahina and M. Onozuka, J. Polymer Sci., <u>A2</u>, 3505, 3515 (1964)
- A. A. Miller, E.J. Lawton and J.S. Balwit, J. Polymer Sci., <u>14</u>, 503 (1964),
   A. A. Miller, J. Phys. Chem., <u>63</u>, 1755 (1959).
- 5. G.J. Atchison, J. Polymer Sci., 49 385 (1961).
- S. Ohnishi, Y. Nakajima and I. Nitta, J. App. Polymer Sci., 24, 629 (1962).
- 7. B.R. Loy, J. Phys. Chem., <u>65</u>, 58 (1961).
- Z. Kuri, H. Ueda and S. Shida, J. Chem. Phys. <u>32</u>, 371 (1960).
- 9. I. Ouchi, J. Polymer Sci., A 3, 2685 (1965).
- 10. G. M. Burnett and R.A. Haldon, European Polymer Journal 3, 449 (1967).
- 11. R.R. Stromberg, S. Straus and B.G. Achhammer, J.Polymer Sci., 35, 355 (1959)
- 12. N. Grassie, Chem.Industry, p. 161,(1954)
- 13. V. Hartmann, Kolloid, Z. 139, 146 (1954) .
- 14. E. J. Arlman, J. Polymer Sci., <u>12</u>, 547 (1954).
- 15. G. Talamini, and G. Pezzin, Makromolek Chem. <u>39</u>, 26, (1960).
- 16. W. I. Bengough and H.M. Sharpe, Makromolek Chem., <u>66</u>, 31,45 (1963).
- 17. A. Crosato-Arnaldi, G. Palma, E. Peggion and G. Talamini, J. App. Polymer Sci., 8, 747, (1964).
- 18. L. Valko, I. Tvaroska, IUPAC, International Symposium on Macromolecular Chem., Budapest, preprint 1969, p.181, Vol.5.

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- 20. D.H.R. Barton and P.F. Onyon, Trans Faraday Soc., 45, 725 (1949).
- 21. D.H.R. Barton, and K.E. Howlett, J. Chem. Soc., 155, (1949).
- 22. E.W.R. Steacie, "Atomic and Free Radical Reactions", Am. Chem. Soc., Monographs, <u>102</u>, (1946) Chapter IX.
- 23. D.E. Winkler, J. Polymer Sci., <u>35</u>, 3 (1959).
- 24. P. Bradt and F.L. Mohler, J. Res. Nat. Bur. Stand. 55, 323, (1955).
- 25. B.P. Tikhomirov, H.B. Hopfenberg, V.Stannett and J. J. Williams, Makromolek Chem. <u>118</u>, 177 (1968).
- 26. A. Nakajima and K. Kato, Makromolek Chem., <u>95</u>, 52, (1966).
- 27. J.V. Koleske and L.H. Wartman, "Poly(vinyl chloride)", Gordon and Breach Science Publishers, New York, p.62,(1969).

28. J.H. Knox and R.L. Nelson, Trans. Faraday Soc., <u>55</u>, 937 (1959).

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### CHAPTER V

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EFFECT OF OXYGEN AND ULTRA-VIOLET IRRADIATION ON THE THERMAL DEGRADATION OF POLYVINYL CHLORIDE

#### V-1. INTRODUCTION

In the previous Section, the reaction mechanism for the dehydrohalogenation of PVC in nitrogen was discussed. In the present Chapter, the effect of oxygen and the effect of U.V. irradiation on the thermal degradation are treated.

#### SECTION A

#### V-A. THE EFFECT OF OXYGEN

VA-1

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#### INTRODUCTION

The effect of oxygen on the dehydrochlorination of PVC has been studied by a number of workers (1-11).

Their results can be summarized as follows:

- 1) The dehydrochlorination is accelerated in the presence of  $O_2$ .
- The presence of oxygen causes chain scission during the course of degradation.
- 3) The rate of colour formation is diminished.

In the present work, the effects of an oxygen atmosphere, on radical generation, on HCl evolution and on the kinetic chain lengths for HCl evolution are reported. VA-2

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#### RESULTS

#### VA-2-1. The Effect of Oxygen on the Rates of HCl Evolution and Spin Generation.

Two types of experiments were carried out in the present program. In the first, oxygen was periodically passed over a sample during the thermal degradation of PVC-A in a nitrogen atmosphere. In the second type of experiment, an oxygen atmosphere was present from the beginning of the degradation. Fig. V-1 and Fig. V-2, show the effects of oxygen on HCl evolution and on spin generation, respectively, with the time of heating of sample at 196°C. It is evident, that in the case of HCl evolution (Fig. V-1), there is a much more rapid commencement of the accelerated HCl evolution when the oxygen is present from the beginning.

Figure V-2, shows that this oxygen effect is related to a marked acceleration on the rate of spin generation. The results obtained from Figure V-1, as a first order plot for HCl evolution, are shown in Fig. V-3.

The rates of HCl evolution and spin generation along with the 'g' values, are given in Table V-1. The results from the UV-visible spectra are also included in this Table. Absorption at 400 mµ per mole of HCl evolved are given in the last column of the above Table. Since

## FIGURE V-1

THE EFFECT OF OXYGEN ON THE THERMAL DEHYDROCHLOR-
INATION OF PVC.
SAMPLE: PVC-A, TEMPERATURE: 196 <sup>0</sup> C.
(O) IN A NITROGEN ATMOSPHERE,
(A) IN AN OXYGEN ATMOSPHERE
(X) WHEN OXYGEN WAS PASSED OVER PARTIALLY DEGRADED
SAMPLE IN NITROGEN ATMOSPHERE AT POINT P.

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#### FIGURE V-2

THE EFFECT OF OXYGEN ON SPIN GENERATION BY THERMAL DEGRADATION OF PVC. SAMPLE PVC-A , TEMPERATURE: 196°C. (O) IN A NITROGEN ATMOSPHERE,

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- ( $\Delta$ ) IN AN OXYGEN ATMOSPHERE
- (X) WHEN OXYGEN WAS INTRODUCED INTO PARTIALLY DEGRADED SAMPLE AT POINT P.

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### FIGURE V-3

FIRST ORDER PLOT FOR THERMAL DEHYDROCHLORINA-TION OF PVC IN THE PRESENCE OF OXYGEN. SAMPLE PVC-A , TEMPERATURE:  $196^{\circ}$ C. (O) IN A NITROGEN ATMOSPHERE ( $\Delta$ ) IN AN OXYGEN ATMOSPHERE

(X) WHEN OXYGEN WAS INTRODUCED AFTER 175 MINUTES.

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$\frac{\begin{array}{c} \text{Reaction} \\ \text{Atmosphere} \\ \frac{\text{dHCl}}{\text{dt}} \times 10^8 \\ \text{moles/g./sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{dSpin}}{\text{dt}} \times 10^{12} \\ \text{moles/g./sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{dSpin}}{\text{dt}} \times 10^{12} \\ \text{moles/g./sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{v} = (\text{Kinetic} \\ \text{chain} \\ \text{length} \\ \times 10^{-4} \\ \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \\ \text{sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \\ \text{sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \\ \text{sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \\ \text{sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \\ \text{sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \\ \text{sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \\ \text{sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \\ \text{sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \\ \text{sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \\ \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \end{array} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \end{array} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \end{array} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \\ \text{sec.} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \end{array} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \end{array} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \end{array} \end{array} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \end{array} \end{array} \end{array} $ } \frac{\begin{array}{c} \text{sec.} \end{array} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \end{array} \end{array} \\ \frac{\begin{array}{c} \text{sec.} \end{array} \end{array} \end{array}  } \frac{\begin{array}{c} \text{sec.} \end{array} \end{array} \end{array}  } \frac{\begin{array}{c} \text{sec.} \end{array} \end{array}  } \frac{\begin{array}{c} \text{sec.} \end{array} \end{array}  } \frac{\begin{array}{c}		EFFECT OF OXYGEN	N ON THE RATES (	OF DEGRADATI	ON OF PV	C HEATED AT	196 <sup>0</sup> C.
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	Reaction Atmosphere	(1) $\frac{dHC1}{dt} \times 10^{8}$ moles/g./sec.	(1) $\frac{dSpin}{dt} \times 10^{12}$ moles/g./sec.	ν=(Kinetic chain length) x 10 <sup>-4</sup>	(2) K x 10 <sup>5</sup> Sec. <sup>-1</sup>	(3 <u>)</u> g	(4) A <sub>400</sub> x 10 <sup>-4</sup> /moles of HCl evolved.
0 <sup>(5)</sup> dur- ing deg.) 20.7 4.8 3.0 2.0036±.0003 1.0	N2	36.8	0.66	54.2	1.4	2.0026±.0003	1.7
	0 <sup>(5)</sup> dur- ing deg.	100.0	20.7	4.8	3.0	2.0036±.0003	1.0
<sup>0</sup> 2 65.0 18.00 3.6 2.0	°2	65.0	18.00	3.6	2.0		

TABLE V-1

1)	The rates are calculated from the linear portion of the curves (Fig. V-1 and V-2).
2)	K : First order rate constants for HCl evolution (Fig. V-3)
3)	'g': 'g' value of the E.S.R. signal.
4)	$A_{400}$ : Absorption at 400 mµ per mole of HCl evolved.
5)	Oxygen was introduced after 175 minutes.

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oxygen causes such a pronounced acceleration, it was necessary to degrade the PVC samples at much lower temperatures, than were utilized in the pure N<sub>2</sub> degradation studies (Chapter IV). Therefore, due to a lack of sufficient degree of degradation, the slopes of the linear portion of the curves, Figs. V-1 and V-2, were used, instead of the slopes at 10% degradation.

## VA-2-2 The Effect of 0, on Crosslinking.

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A powdered sample of PVC-A was heated in  $N_2$ and  $O_2$  atmospheres, at  $190^{\circ}\pm 2^{\circ}$ C. At definite intervals of time, small amounts of the degraded samples were removed and mixed with cyclohexanone. These mixtures were stirred at  $90^{\circ}$ C. for 3 days, after which the solutions were filtered. The insoluble materials, which were crosslinked polymer, were dried under vacuum at  $60^{\circ}$ C. to constant weight. From the weight of the soluble sample and the weight of the insoluble residue, the percentages of crosslinked material were calculated. These degraded samples were also analyzed for chlorine percentage, giving a measure of the extent of dehydrochlorination of PVC.

In Fig. V-4, the percentage of crosslinked material obtained vs. time of heating, are plotted. This figure shows that in an oxygen atmosphere the crosslinking started only after three hours, while in the nitrogen atmosphere, at this same time, 53% of the total crosslinked

## FIGURE V-4

CROSSLINKING WITH TIME OF HEATING.

SAMPLE PVC-A, TEMPERATURE: 190  $\pm$  2<sup>o</sup>C.

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- (O) IN A NITROGEN ATMOSPHERE,
- ( $\Delta$ ) IN AN OXYGEN ATMOSPHERE.

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materials was present. In Fig. V-5, the percentage of of Cl loss, in N<sub>2</sub> and crosslinked material vs. સ્ O2 atmospheres are plotted. In the case of nitrogen, crosslinked material increased rapidly, relative to the chlorine loss throughout nearly the whole reaction time. In the presence of oxygen, however, the increase of crosslinked material was just the reverse of that in nitrogen. In this case, no crosslinked material was obtained up to 18% of chlorine loss, while after that it increased very rapidly. The comparison of chlorine losses at any degree of crosslinking reveals that in oxygen, the chlorine loss is considerably higher when compared to degradation in nitrogen atmosphere. At 90% crosslinking, the corresponding values of chlorine loss in nitrogen and oxygen atmosphere were found to be 5 and 40% respectively.

### VA-2-3 The Effect of Oxygen on the I.R. and U.V. Spectra

I.R. and U.V. spectra measurements were made on the same film of Sample PVC-A.

The PVC films were prepared by pouring a dichloroethane solution of polymer onto a glass plate. The solvent was then evaporated and the film was dried under vacuum at  $70^{\circ}$ C. for two weeks. The film was then placed between two microscope slides in the center of which small holes had been drilled. These plates were then placed in the degradation apparatus, which was heated above the Tg (86°C) for 5

### FIGURE V-5

CROSSLINKING VS. CHLORINE LOSS. SAMPLE PVC-A , TEMPERATURE: 190 ± 2<sup>O</sup>C. (O) IN A NITROGEN ATMOSPHERE

( $\Delta$ ) IN AN OXYGEN ATMOSPHERE.

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minutes, following this, they were cooled to room temperature. This whole operation was done under an N2 atmos-The U.V. and I.R. spectra were then recorded phere. UNICAM 800 and Perkin Elmer 521 instruments, on respectively. To effect degradation, the samples were heated in an  $N_2$  or  $O_2$  atmosphere, at 160 ± 5°C., with the flowing gas acting as a carrier gas for HCl. The HCl evolution was measured by the conductivity method in the usual manner. The U.V. spectra were recorded after definite intervals of heating, while the I.R. spectra were recorded only after the final heating. Since the PVC became opaque to U.V. (and visible) light after long heating times, only the initial stage of dehydrochlorination (up to 3%) could be studied.

# VA-2-3-i I.R. Spectral Changes

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Because PVC-A was prepared using benzoyl peroxide as an initiator, the undegraded samples showed small extra bands at 1730, 1765, and at  $1785 \text{ cm}^{-1}$ . The bands at 1785 and  $1765 \text{ cm}^{-1}$  were assigned to the carbonyl vibration of the catalyst benzoyl peroxide<sup>(12)</sup>, while the one at  $1730 \text{ cm}^{-1}$  is thought to be due to the carbonyl stretching vibrations of keto and aldehyde groups derived from the decomposition of benzoyl peroxide. When the film was heated in nitrogen the bands at 1785 and  $1760 \text{ cm}^{-1}$ disappeared, suggesting that the catalyst, which was
present as an impurity in PVC, was decomposed. When the film was heated in an oxygen atmosphere, the degraded material exhibited a broad absorption in the 1500-1900 cm<sup>-1</sup> region. The I.R. spectra in this region are shown in Figure V-6. The bands at 1785, 1760, and at 1730 cm<sup>-1</sup> disappeared and a broad band appeared in this region, as is shown in Figure V-6. This behaviour suggests that in the presence of  $O_2$ , carbonyl structures are formed.

# VA-2-3-ii U.V.Visible Spectral Change

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The UV spectral changes associated with degradation of PVC-A in nitrogen and oxygen atmospheres are shown in Figure V-7. The absorption at 400 mµ,  $(A_{400})$ , (which is the absorption for about 5 conjugated double bonds), vs. HCl evolution are plotted. The absorption at 400 mµ per mole of HCl evolved are calculated from this figure, and are given in Table V-1. The results show that in case of oxygen, the absorption at 400 mµ per mole of HCl evolved is less than that in a nitrogen atmosphere.

## VA-2-4 The Effect of Oxygen on Free Radicals Generated by Heating PVC-A in N<sub>2</sub> Atmosphere.

The 'g' values of the E.S.R. spectra, for the signals generated in the presence of nitrogen and oxygen were given in Table V-1. The change in g values of the spectra shows that in the presence of oxygen, the radicals are different. The nature of the radicals

## FIGURE V-6

THE EFFECT OF OXYGEN ON INFRA-RED SPECTRAL CHANGE.

SAMPLE: PVC-A , TEMPERATURE: 160 ± 5°C. (----) BEFORE HEATING, (-.-.-) HEATED IN NITROGEN. (----) HEATED IN OXYGEN.

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# FIGURE V-7

HC1 EVOLUTION WITH ABSORPTION AT 400 MM. SAMPLE PVC-A; TEMPERATURE:  $160 \pm 5^{\circ}C$ . (0) IN NITROGEN

( $\Delta$ ) IN OXYGEN.

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produced by the interaction of oxygen will be discussed in a later section.

To determine the effect of oxygen on the rate of radical production, polymer sample PVC-A was partially degraded in a nitrogen atmosphere at 250°C., and then cooled to room temperature. The E.S.R. spectrum was measured at room temperature in the nitrogen atmosphere, and then oxygen was passed into the sample at the same flow rate as that of the N2. The changes in the spectra with the time of oxygen flow were recorded. After some time, the oxygen was replaced by nitrogen gas and again the spectra with time of gas flow were measured. In Figure V-8, the change in spin concentrations due to the interaction of In oxygen, at room radicals with oxygen are plotted. temperature, the radical concentration is seen to rise. When the oxygen is cut off at point Y there is a gradual diminution which is reversed when oxygen is reintroduced at 'Z'. The effect of oxygen on spin generation is thus a reversible process.

## VA-2-5 Decay, at Room Temperature, of the Radicals Formed in the Presence of Oxygen.

Two samples were heated at 215°C. in an oxygen atmosphere, and then cooled to room temperature. One of the degraded samples was sealed in a nitrogen atmosphere, and the other was exposed to air. The signal intensities obtained from these samples vs. time in days at

### FIGURE V-8

EFFECT OF OXYGEN, AT ROOM TEMPERATURE, ON THE SPINS, ALREADY GENERATED BY HEATING PVC-A, AT 250<sup>O</sup>C.IN A NITROGEN ATMOSPHERE.

AT POINT 'X' OXYGEN WAS PASSED, AT POINT 'Y'. OXYGEN WAS REPLACED BY NITROGEN AT THE SAME FLOW RATE; AT POINT 'Z' NITROGEN WAS REPLACED BY OXYGEN, AGAIN AT THE SAME FLOW RATE. THE ATMOS-PHERE CHANGES WERE DONE AT ROOM TEMPERATURE.

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SPIN PER GRAM PVC  $\times$  10<sup>-15</sup>

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room temperature are plotted in Figure V-9. The figure shows that the sample exposed to air does not decay to the same low value as that of the  $N_2$  sample.

#### VA-3 DISCUSSION

## VA-3-1 The Interaction of Oxygen With Radical

From the results described thus far, a number of patterns are apparent:

- In the presence of oxygen, the rates of HCl evolution and spin generation both increase.
   Section VA-2-1.
- 2) The change in 'g' values, suggests that in oxygen a different kind of radical, a peroxy, is formed. The formation of these peroxy radicals depends on the pressure of oxygen and shows that the radical generation is a reversible process. This may be explained as follows, in the light of Ingram's explanation<sup>(13)</sup>.

There may be the chemical interaction of oxygen molecules with the free radicals. It is possible for the oxygen to form a chemical bond with the free radical electrons, and it is also possible to break these bonds by just reducing the pressure of  $O_2$  or replacing it by  $N_2$ ."

## FIGURE V-9

ROOM TEMPERATURE DECAY OF RADICALS GENERATED BY HEATING PVC-A IN AN OXYGEN ATMOSPHERE AT 215<sup>O</sup>C.

(O) DECAY IN AIR;

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( $\Delta$ ) DECAY IN NITROGEN.



TIME, DAYS

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It is also noted that these peroxy radicals were found to decay slightly faster in air, than in an inert atmosphere (Fig. V-9). Both of these observations further support the formation of peroxy radicals in the presence of oxygen. - Sections VA-2-1, VA-2-4 and VA-2-5.

- 3) A reduction in crosslinking and a reduction in kinetic chain length occur. - Sections VA-2-1 and VA-2-2.
- Infra-red spectra show the presence of a carbonyl group in the oxygen degraded material.

These results must now be rationalized in terms of the reaction scheme discussed in Chapter IV. Let us look at the reactions which are possible between oxygen and radicals proposed in the degradation scheme outlined in Chapter IV. These radicals are

 $-CH_{2}-CH-CH_{2}-CHCl- - from reaction (IV-4)$   $[R_{1} \cdot ]$   $-CH-CHCl-CH_{2}-CHCl- - from reaction (IV-5 and IV-6)$   $[R_{2} ] IV-6)$   $-CH_{2}-CCl-CH_{2}-CHCl- - from reaction (IV-9)$   $[R_{1}']$ 

Let us first consider the reaction of oxygen

with the  $R_1^{\bullet}$  radical.

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$$-CH_2-CH-CH_2-CHCl-+ \circ_2 \longrightarrow -CH_2-CH_2-CHCl- (V-1)$$

This peroxy radical can now abstract hydrogen atoms from another PVC molecule yielding an  $R_2$  radical and an unstable hydroperoxide.

$$-CH_{2} \xrightarrow{-CH}_{O} -CH_{2}CHCl + R_{2}H \xrightarrow{-CH}_{O} -CH_{2} \xrightarrow{-CH}_{O} -CH_{2} \xrightarrow{-CH}_{O} -CHCl + R_{2}$$

The  $R_2$  radical will then undergo the degradation scheme shown in Chapter IV, reaction (IV-4) to (IV-9), while the hydroperoxide can decompose to generate new radicals which will in turn, initiate new decomposition chains in the following manner.



By this route, radical  $R_1$  which by the degradation scheme is not important in the decomposition of PVC in a nitrogen atmosphere, is shown here to be converted into  $R_2^{\bullet}$  and  $Cl \cdot radicals$ , which are propagating species. Furthermore, a hydroxyl radical,  $OH \cdot$ , is obtained, which is able to generate still another  $R_2^{\bullet}$  radical. Similarly,  $R_1^{\bullet}$  radical generated in the termination step (IV-9) can yield similarly active species  $R_2^{\bullet}$ ,  $Cl \cdot$  and  $OH \cdot$ .

A similar reaction of oxygen with  $R_2$  can be merely a chain transfer reaction, but may cause also acceleration by OH· generation. The net result is that by the reaction of oxygen with the radicals, there will be an increase in the number of chains propagating and thus an increase in the rate of HCl evolution. The side reaction of chain scissioning and carbonyl formation is shown in reaction (V-4).

A contribution to the observed acceleration in dehydrochlorination which is not proven but which can also be postulated, may be due to the ease of diffusion of "small" radicals such as OH. through the PVC matrix.

# VA-3-2 The Interaction of Oxygen with Conjugated Polyene.

A second mechanism for radical generation can be postulated on the basis of Figure V-8, where oxygen was shown to increase the radical concentration in a reversible way. Besides the Ingram explanation, this can also be interpreted as a direct attack of oxygen on the conjugated polyene.

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Indeed, polyolefins have been shown to be easily attacked by oxygen<sup>(14)</sup>. This attack of oxygen can diminish the length of the conjugated polyene sequences resulting in a bleaching action by oxygen and creating new propagating radicals. Druesdow and Gribbs<sup>(1)</sup> proposed the following mechanism for this reaction.

Attack of Oxygen on a Polyene

$$-CH=CH-CH=CH-+O_2 \xrightarrow{H H H H H} -C-C-C=C-C- (V-6)$$

Radical Generation

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The peroxy radicals produced in the above reaction can either initiate new chains, by abstracting hydrogen from PVC molecule in the manner previously discussed in Chapter (IV), or can undergo a reaction scheme similar to that shown in reactions (V-2) to (V-5).

The results in Table V-1 show that  $\frac{dHC1}{dt}$ underwent a greater acceleration when  $O_2$  was introduced during the degradation of PVC than when  $O_2$  was present from the beginning.When  $O_2$  is used from the beginning, only the interaction between oxygen and radicals can take place. However, when oxygen is introduced during degradation, in addition to the interaction between  $O_2$  and free radicals, the attack of  $O_2$  on polyene also occurs. This second reaction yields additional radicals in the manner described. Furthermore, in the degraded PVC the number of  $R_1$ ' inactive radicals, will be greater than in an undegraded sample. These also, can react with  $O_2$  and produce propagating species  $R_2$  and Cl. Each  $R_1$ ' "inactive" radical could produce, by this route,  $2R_2$  and one Cl. "active" radicals. Such reactions explain the larger rate of dehydrochlorination when oxygen was passed over partially degraded PVC.

### VA-4 SUMMARY AND CONCLUSIONS

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The effect of oxygen on the degradation of PVC has been studied. The following results were obtained:

- In oxygen the rates of HCl evolution and spin generation were increased.
- 2) When oxygen was introduced during degradation, the  $\frac{dHC1}{dt}$  and  $\frac{dSpin}{dt}$  were found to be higher than when oxygen was present from the beginning.
- Samples heated in an oxygen atmosphere contained carbonyl groups.

On the basis of these results, a mechanism for

the effect of oxygen on the degradation of PVC is proposed. This mechanism was based on the reaction of oxygen with radicals, generated in PVC, to form unstable peroxy radicals. In addition to this, it is proposed that oxygen reacts directly with conjugated polyenes to form peroxide linkage.

#### SECTION B

#### V-B. THE EFFECT OF ULTRA-VIOLET IRRADIATION ON THE THERMAL DEGRADATION OF PVC.

VB-1.

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#### INTRODUCTION

Polyvinyl chloride has been found to decompose during irradiation by U.V. light in the wavelength region of 2700-3000<sup>O</sup>A. This is, at first, a surprising reaction since Kenyon<sup>(2)</sup>, who studied the photo decomposition of alkylchlorides, showed that they were stable to U.V. light until the region of  $2300-2200^{O}A$ . is reached. However, in a subsequent study, utilizing impure secondary butyl chloride, he found that at  $2700^{O}A$ , he could initiate decomposition. According to him, CH<sub>3</sub> radicals obtained by absorbing impurities, such as acetone, induce the decomposition of secondary butyl chloride

 $CH_3COCH_3 \xrightarrow{hv} 2CH_3 + CO$  (V-8)

Impurities, such as ketones, can be expected to be present in peroxide initiated polyvinylchloride and hence, 2700<sup>O</sup>A. wavelength initiation is reasonable. Indeed, Kenyon<sup>(2)</sup> has done a short investigation with macromolecules and shown that PVC pre-irradiated at room temperature with U.V. rays does indeed, undergo an accelerated rate of decomposition. In the present work, this pre-irradiated experiment was repeated and measurements were made on both the rates of thermal dehydrochlorination and of spin generation. The activation energies associated with these processes were also determined.

#### VB-2 EXPERIMENTAL

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#### VB-2-1 Irradiation of PVC Sample

Polyvinyl chloride Sample A was irradiated for 1, 2 and 3 hours by U.V. rays, at room temperature in air. For this purpose, a photochemical quartz lamp (obtained from Ultra Violet Products, Inc., California), shaped as a flat grid was used. This lamp emitted a high percentage (85%) of U.V. at a wavelength of 2537°A. E.S.R.-HCl measurements were carried out on these preirradiated samples.

#### VB-2-2 E.S.R. - HCl Evolution Measurements

The techniques utilized are discussed in Chapter III.

#### VB-3 RESULTS AND DISCUSSION

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The pre-irradiated samples (irradiated for 1,  $2\frac{1}{4}$  and 3 hours at room temperature) were thermally degraded at  $200^{\circ}$ C. in nitrogen atmosphere, inside the E.S.R. instrument cavity. The data obtained by HCl evolution and spin generation are plotted the usual way, in Figs. V-10 and V-11, respectively. The curves for samples irradiated for  $2\frac{1}{4}$  and 3 hours are divided into two portions, due to two different slopes. In this case, these slopes of the linear portions of the curves are taken as the initial and final rates for HCl evolution and spin generation.

The pre-irradiated samples showed the presence of some free radicals at zero time of heating. The activation energies for HCl evolution and spin generation were determined for the sample, which was irradiated for 2<sup>1</sup>/<sub>4</sub> hours. The samples were heated from 212<sup>0</sup> to 231<sup>0</sup>C., in nitrogen atmosphere, and the rates were used in the calculation of activation energies. The rates and activation energies for the HCl evolution and spin generation are summarized in Table V-2.

This Table shows that with increased time of pre-irradiation, the rate of HCl evolution and spin generation were increased. Furthermore, U.V. irradiation reduces the kinetic chain length. The increase in  $\frac{dSpin}{dt}$  and the

## FIGURE V-10

THE EFFECT OF U.V. IRRADIATION ON THERMAL DEHYDRO-CHLORINATION OF PVC-A. TEMPERATURE:  $200^{\circ}$ C, ATMOSPHERE:  $N_2$ (O) WITHOUT U.V. IRRADIATION, ( $\Delta$ ) U.V. IRRADIATION FOR 1 HOUR, (X) U.V. IRRADIATION FOR 2<sup>1</sup>/<sub>4</sub> HOURS, ( $\Box$ ) U.V. IRRADIATION FOR 3 HOURS.

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## FIGURE V-11

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THE EFFECT OF U.V. IRRADIATION ON SPIN GENERATION OF SAMPLE PVC-A. TEMPERATURE:  $200^{\circ}$ C, ATMOSPHERE: NITROGEN (O) WITHOUT U.V. IRRADIATION, ( $\Delta$ ) U.V. IRRADIATION FOR 1 HOUR (X) U.V. IRRADIATION FOR 2<sup>1</sup>/<sub>4</sub> HOURS, ( $\Box$ ) U.V. IRRADIATION FOR 3 HOURS.

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TAB	LE	V-	2	
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RESULTS	OF	U.V.	IRRADIATED	SAMPLE	(PVC-A)
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Temp.in <sup>O</sup> C.	Time of U.V. Irradiation (hr) at room Temperature.	<u>dHC1</u> x 10 <sup>8</sup> moles/g./sec.	<u>dSpin</u> x 10 <sup>12</sup> dt moles/g./sec.	ν x 10 <sup>-4</sup>	E <sub>HCl</sub> Kcal	<sup>E</sup> spin /mole	HCl at 320 mins. x10 <sup>4</sup> mole/g.
200 200 200	O l 21 init- ial	7.44 <sup>(a)</sup> 25.7 6.36	.36 <sup>(a)</sup> .56 .72	20.2 45.2 8.77	26±1	56±3	2.75 19.5 22.5
200	" final 3 init- ial " final 2 <sup>1</sup> / <sub>2</sub>	23.7 6.63 34.64 37.5	2.24 .92 2.76 .97	10.6 7.2 12.52 38.66	28±6	46±10	36.5
221.5 231.5	2 <del>1</del> 2 <del>1</del>	108.69 135.6	5.6 6.2	19.4 21.9			

(a) This rate is at 3% degradation.

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reduction in kinetic chain length suggest that the U.V. acts by increasing the rate of initiation. The presence of free radicals at zero time of heating indicates the production of free radicals by this pre-irradiation. There may also be some unsaturation present at zero time, due to the partial degradation of PVC by irradiation. This was not, however, detected in U.V. spectra of the irradiat-The activation energy for the dehydrochlorinaed material. tion was found to be approximately the same as that of the unirradiated samples, but E spin for the irradiated sample was somewhat lower, being 46 Kcal/mole, for the irradiated sample, as compared to 56 Kcal/mole for the unirradiated one. This reduction in E spin is thought to be due to the fact that the initiation step was aided by the previously mentioned action of U.V. irradiation. The role of the radicals produced is obvious, while the presence of double bonds in the partially degraded material will make available allylically activated C-Cl bond. Valko and Tvaroska<sup>(15)</sup>, have shown that the C-Cl bond strengths in such unsaturated chlorocompounds are substantially lower than those in the saturated materials.

#### VB-4 SUMMARY AND CONCLUSIONS

The effect of pre-irradiation by U.V. rays on the thermal degradation of PVC has been studied. It was found that:

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- 1) The  $\frac{dHCl}{dt}$  and  $\frac{dSpin}{dt}$  increased with the time of pre-irradiation.
- 2) The activation energy for HCl evolution was unaffected by pre-irradiation, but the activation energy for spin generation was somewhat reduced.

On the basis of the above results, it was concluded that pre-irradiation facilitates the initiation step in the decomposition reaction.

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## V-A-B REFERENCES

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1.	D. Druesdow and C.F. Gibbs, Natl. Bur.Stand. Circular 525, 69 (1953)
2.	A.S. Kenyon, Natl.Bur.Stand., Circular, 525, 81 (1953)
3.	E.J. Arlman, J. Polymer Sci., <u>12</u> , 543, (1954).
4.	B. Baum and L.H.Wartman, J. Polymer Sci., <u>28</u> , 537 (1958).
5.	G. Talamini and G. Pezzin, Makromolek.Chem., <u>39</u> , 26 (1960).
6.	B. Dolezel and J. Stepek, Chem. Prumysl, <u>10</u> , 381 (1960).
7.	B. Baum, S.P.E.J., <u>17</u> , 71 (1961).
8.	A. Rieche, A. Grimm and H. Mucke,Kunstoffe, <u>52</u> , 265 (1962).
9.	W.I. Bengough and H.M. Sharpe, Makromolek. Chem., 66, 31, (1963).
10.	M. Lisy, Chem. Zvesti, <u>19</u> , 84 (1965).
11.	D.E. Winkler, J. Polymer Sci., <u>35</u> , 3 (1959).
12.	Bellamy, C.C., "The Infra-Red Spectra of Complex Molecules" (1958) Second Edition, Methuen, London. Chapters IX and X.
13.	D.J.E. Ingram, "Free Radicals as Studied by Electron Spin Resonance" (1950), Butterworths Scientific Publications, p.212.
14.	E.H. Farmer, Symposium on Oxidation, Trans Faraday, Soc. <u>42</u> , 228 (1946)
15.	L. Valko, I. Tvaroska and IVPAC, International Symp. on Macromolecular Chemistry, Budapest, Preprint, Vol.5, 181 (1969).

## CHAPTER VI

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# THE EFFECT OF STABILIZERS ON THE DEGRADA-TION OF POLYVINYL CHLORIDE

#### VI-1 INTRODUCTION

In the preceding last two Chapters of this thesis, the mechanisms of thermal degradation of PVC have been discussed. In the present Chapter, the results of an investigation into the effects of organo-tin stabilizers on the thermal dehydrochlorination will be presented.

On the basis of the mechanism which we have described in previous chapters, an ideal stabilizer of PVC should act in the following ways:

- It should act as a scavenger for the radicals produced during the degradation of PVC, in order to lower the rate of degradation.
- 2) Since colour formation is associated with a long conjugated double bond segment, it should also be capable of reacting with the double bonds, in order to break up the sequences, and thus lower the amount of the colour.

In addition to the above, a few other properties are also required for practical applications and for ease in processing. These are :

 The stabilizer should be opaque to U.V. light.

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2) It should act as an antioxidant.

3) It should be chemically inert to the processing equipment and ingredients, such as plasticizers, etc.

## VI-2. CHOICE OF STABILIZER

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The stabilizers most widely used commercially can be classified into two main groups:

- Metallic salts of inorganic and organic acids,
   e.g. Lead silicate, stearates of Ca, Cd and
   Pb, etc.
- Organometallic compounds, mostly organotin compounds.

In addition to these two groups, a number of epoxides and esters have also been employed.

Indeed, commercial PVC compound usually has 3 to 4 stabilizers present and as a result, it is difficult to identify the role of each.

In the present studies we have used only one stabilizer at any time, this being a member of a series of organotin compounds of structure  $R_X SnY_{4-X}$ . R is an alkyl group and Y is a carboxylate group connected to the tin atom by a Sn-O bond.

Frye and Horst<sup>(1)</sup>, in 1964, postulated that PVC stabilization by organotin compounds resulted from the replacement of labile chlorine atoms in the polymers by the Y group of the stabilizer  $(C_4H_9)_X SnY_{4-x}$ . This proposal would mean that in series of organotin compounds of varying x, that is, dibutyltin dilaurate (x=2), tributyltin laurate (x=3) and tetrabutyltin (x=4), the tetrabutyltin, where the Y group is absent, should exert no stabilizing effect. In the present work, these compounds are used for testing this theory, and in addition, organotin compounds with various Y groups, (dibutyltin dilaurate, maleate and diacetate) were employed.

## VI-3 THE EVALUATION OF STABILIZER EFFICIENCY

#### VI-3-1 Introduction

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In evaluating the efficiency of a stabilizer, one of the first factors which must be considered is the dispersion of the stabilizer in the PVC. The degree of dispersity is determined by the physical properties of the stabilizer, its compatibility with PVC and the method of mixing. The stabilizing efficiencies of various agents have been found to be a function of the manner in which they have been dispersed. Thus, in order to compare the stabilizing action of different chemicals, it is necessary that they be mixed with the polymer under identical conditions. For the evaluation of stabilizer efficiency, the following methods have been used by various workers.

# VI-3-2 Decomposition Temperature Method

In this method, a set of "dynamic thermogravimetric" curves of PVC resin with and without stabilizers are utilized. The decomposition temperatures obtained from these curves are then compared (2-4).

# VI-3-3 Induction Period Method

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Pure PVC and a PVC containing a stabilizer are heated under identical experimental conditions, with respect to temperature, atmosphere, etc., and the differences in the induction periods are determined<sup>(2,3)</sup>.

# VI-3-4 <u>Methods based on the "Colour Change" of</u> the Sample.

Methods based on "colour change" of the samples can be divided into two general classes:

- (i) Fundamental Method: In this method the
   UV<sup>(4)</sup> and visible spectra before and after heat ing of the PVC samples with and without stabiliz er are compared.
- (ii) Technological Method: In this method, the sample films are heated at a certain temperature for a definite time and the colour changes are

compared visually (5-7).

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## VI-3-5 Method Based on HCl Evolution.

By measuring the amounts and the rates of HCl evolved under identical conditions of degradation<sup>(5,8)</sup>, and then comparing the rate constants obtained for pure samples, and for the samples containing stabilizers, comparison can then be made by using a term  $\theta$  for stabilizer efficiency. The term  $\theta$  can be defined as

$$\theta = \frac{K_{O} - K_{S}}{K_{O}}$$

where  $K_0$  is the first order rate constant for the dehydrochlorination of pure PVC and  $K_s$  is the first order rate constant for the sample containing stabilizer. For the ideal stabilizer  $K_s$  should be zero and  $\theta$  should be equal to one. Thus, the efficiency of a stabilizer as expressed in these terms, will range from 0 to 1.

In the present work, this method based on HCl evolution was employed and, in addition, the effect of stabilizer on the rate of spin generation and the spectral changes were also determined.

#### VI-4. EXPERIMENTAL

## VI-4-1 Dispersion of Stabilizer in PVC-A Resin

The dispersion of the stabilizer in PVC resin

can be achieved by the following methods:

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- By mixing the solutions of stabilizer and resin and evaporating the solvents. In this case, a film of the polymer is obtained.
- 2) By dissolving stabilizer in a solvent which is a non-solvent for the resin and shaking it with powdered PVC and then evaporating the solvent.
- 3) By shaking a suspension of stabilizer and resin (if the stabilizer is not soluble in common solvents) in some liquid media.

In the first case, the dispersion of stabilizer will be uniform, while in the second case, the adsorption of stabilizer at the surface of resin particle will take place. Although the first method is desirable, a uniform packing of sample in E.S.R. is required, and thus, a powdered sample is preferred. In view of this, in the present work, the second method of dispersion had to be employed.

Weighed quantities of stabilizer and powdered PVC-A of 40-60 mesh particle size were shaken in the presence of petroleum ether  $(60-80^{\circ}C)$ , a solvent for the stabilizer and non-solvent for PVC, for 4 to 5 hours. The petroleum ether was then evaporated by flash evaporation in vacuum at 50-60°C. The stabilizer containing polymer samples were maintained at 75°C. in a vacuum oven for one day, in order to remove the last of the solvent. Finally, the samples were dried by keeping them in vacuum for 2-3 days.

VI-4-2 E.S.R. - HCl Evolution Measurements

The techniques utilized were identical to those discussed in Chapter III.

VI-4 RESULTS

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VI-5-1 The Effect of Changing 'x' oin Compounds of Structure  $(C_4H_9)_x Sn[oC(CH_2)_{10}CH_3]_{4-x}$ on the Stabilizer Activity.

For this purpose, the following compounds were

used:

Compound	Structure	Value of x
Dibutyltin Dilaurate	(C <sub>4</sub> H <sub>9</sub> ) 2 <sup>Sn[OC(CH<sub>2</sub>)</sup> 10 <sup>CH</sup> 3 <sup>]</sup> 2	x = 2
Tributyltin Laurate	$(C_4H_9)_{3} sn[OC(CH_2)_{10}CH_3]_1$	x = 3
Tetrabutyltin	$(C_4H_9)_4Sn$	x = 4

These stabilizers were mixed with PVC-A in the manner described. In every case, the amount of

stabilizer taken was  $5.7 \times 10^{-3}$  moles per 100 g. of PVC-A. The HCl evolution and spin generation with time of heating are given in Figures VI-1 and VI-2. Fig. VI-1

## FIGURE VI-1

THE EFFECT OF ORGANOTIN STABILIZER WITH VARIOUS VALUES OF X IN STRUCTURE  $R_x SnY_{4-x}$ , ON THE RATES OF HC1 EVOLUTION.

SAMPLE: PVC-A ; TEMPERATURE: 239 ± 1°C.
ATMOSPHERE: NITROGEN,
CONCENTRATION OF STABILIZER: 5.7 x 10<sup>-3</sup> MOLES/100 G.PVC-A
(O) PURE PVC-A ;

(X) PVC-A + DIBUTYLTIN DILAURATE

(Δ) PVC-A + TRIBUTYLTIN LAURATE

( ) PVC-A + TETRABUTYLTIN

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### FIGURE VI-2

THE EFFECT OF ORGANOTIN STABILIZER WITH VARIOUS VALUES OF X IN STRUCTURE  $R_x SnY_{4-x}$ , ON THE RATES OF SPIN GENERATION.

SAMPLE: PVC-A ; TEMPERATURE:  $239 \pm 1^{\circ}C$ . ATMOSPHERE: NITROGEN, CONCENTRATION OF STABILIZER: 5.7 x  $10^{-3}$  MOLES/100 G.PVC-A

(O) PURE PVC-A ;

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(X) PVC-A + DIBUTYLTIN DILAURATE

( $\Delta$ ) PVC-A + TRIBUTYLTIN LAURATE

(
) PVC-A + TETRABUTYLTIN

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shows that the efficiencies of the stabilizers are in the following order:

Tetrabutyltin > Tributyltin > Dibutyltin Laurate > Dilaurate

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Another factor from Figures VI-1 and VI-2 is that, over the reaction period studied, two slopes are evident in case of dibutyltin dilaurate, whereas, tributyltin laurate and tetrabutyltin do not show this effect. This same behaviour holds for both the spin generation and the HCl evolution. The rates of HCl evolution and spin generation are calculated from the linear portions of the These rates, as well as  $\theta$  values, are given in curves. Table VI-1. The presence of two slopes, over the reaction period studied, for the dibutyltin dilaurate and the alternative behaviour of tetrabutyltin and tributyltin laurate, indicate that dibutyltin dilaurate is an adequate stabilizer only up to 120 minutes of heating, while the other two are active for longer times. The rates for tributyltin laurate and tetrabutyltin are the same within experimental error. The chain lengths for tributyltin laurate and tetrabutyltin are both lower than in the case of dibutyltin dilaurate.

#### VI-5-2 Effect of Varying the 'y' Groups on the Dehydrochlorination of PVC

The following compounds of carboxylate groups

### TABLE VI-1

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### EFFECT OF NUMBER OF BUTYL GROUPS IN TIN COMPOUND ON THE DEGRADATION RATES AND STABILIZER EFFICIENCIES

Concentration of stabilizer =  $5.7 \times 10^{-3}$  moles/100 g. PVC-A

Sample	Temp <sup>O</sup> C.	d HCl/dt x 10 <sup>8</sup> moles/g./sec.	dSpin/dt x 10 <sup>12</sup> moles/g./sec.	$v = \frac{dHCl}{dSpin} \times 10^{-4}$	K x 10 <sup>5</sup> sec. <sup>-1 .</sup>	$\theta = \frac{K_0 - K_s}{K_0}$
Pure PVC-A	238	447.0	195.3	2.3	11.4	0
PVC-A +	init	ial 50.4	43.0	1.17	1.56	.86
Dibutyl tin dilaurate	fina	1 250.0	83.0	3.01	9.72	0.147
PVC-A + tributyl tin laurate	239	40.1	32.3	1.24	1.20	0.89
PVC-A + Tetra butyltin	238	38.8	25.1	1.54	1.73	. 85

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having different numbers of carbon atoms were investigated. In the case of maleate, a reactive double bond was also a part of the Y group.

Compounds	Structure.	<pre># of Carbon Atoms in 'Y' carboxylata groups.</pre>
Dibutyltin Diacetate	$(C_4H_9)_2 Sn[OCOCH_3]_2$	2 carbon atoms
Dibutyltin Dilaurate	$(C_4H_9)_2 sn[ococ_{11}H_{23}]_2$	12 carbon atoms
Dibutyltin Maleate		<pre>4 carbon atoms + one double bond</pre>

The method of mixing these stabilizers was the same as previously described. In the present case, however, since dibutyltin maleate is not soluble in petroleum ether, it was suspended with PVC in petroleum ether, and the mixture was shaken. The results obtained with these compounds are given in Figures VI-3 and VI-4. In Fig. VI-3, the HCl evolution with time of heating are plotted. From this figure, it is evident that in case of dibutyltin diacetate and dibutyltin dilaurate, two slopes were obtained, while in the case of dibutyltin maleate, only one slope was evident. In Figure VI-4, the first order reaction plots of HCl evolution are given. The rates of HCl evolution, and first order rate constants

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#### FIGURE VI-3

THE EFFECT OF ORGANOTIN STABILIZER WITH DIFFERENT Y GROUPS IN STRUCTURE  $R_x SnY_{4-x}$ , ON THE RATES OF HC1 EVOLUTION.

SAMPLE: PVC-A ; TEMPERATURE:  $242 \pm 1^{\circ}$ C. ATMOSPHERE: NITROGEN, CONCENTRATION OF STABILIZER: 5.7 x  $10^{-3}$  MOLES/100 G.PVC (0) PURE PVC-A ;

- (X) PVC-A + DIBUTYLTIN DILAURATE
- ( $\Delta$ ) PVC-A + DIBUTYLTIN DIACETATE

( ) PVC-A + DIBUTYLTIN MALEATE.

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### FIGURE VI-4

FIRST ORDER REACTION PLOTS FOR HC1 EVOLUTION, WITH COMPOUNDS HAVING DIFFERENT Y GROUPS SAMPLE: PVC-A ; TEMPERATURE:  $242 \pm 1^{\circ}$ C. ATMOSPHERE: NITROGEN, CONCENTRATION OF STABILIZER:  $5.7 \times 10^{-3}$  MOLES/100 G.PVC-A (O) PURE PVC-A ; (X) PVC-A + DIBUTYLTIN DILAURATE ( $\Delta$ ) PVC-A + DIBUTYLTIN DIACETATE

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( ) PVC-A + DIBUTYLTIN MALEATE.

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calculated from the above figures, are given in Table VI-2. The absorptions at 400 m $\mu$  A 400 per mole of HCl evolved, are also included in this Table. Once again, the rates in Column 3 are calculated from the linear portion of the curves. The above Table reveals the fact that the stabilizers act in the following order, if the initial slopes for HCl loss are taken in the cases of dibutyltin dilaurate, and dibutyltin diacetate.

Maleate > Acetate > Laurate VI-5-3 Effect of Stabilizer on Spectral Changes

The infrared and UV-visible spectra were measured on the same stabilized PVC-A film before and after degradation at  $160 \pm 5^{\circ}$ C. in nitrogen atmosphere. The methods of preparation of films and measurement were the same as described in Chapter V. During the preparation of the film, a fixed amount of stabilizer  $(5.7 \times 10^{-3} \text{ moles/g. PVC})$  was added in the solution of PVC-A,from which the film was cast. For this study, dibutyltin diacetate, dibutyltin dilaurate, and dibutyltin maleate stabilizers were used. The U.V.-visible spectra of the PVC films containing stabilizers were measured after certain intervals of heating, but I.R. spectra were measured only before and after heating. The amounts of HCl evolved with time of heating were also recorded.

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### TABLE VI-2

# EFFECT OF VARIOUS Y GROUPS ON STABILIZER ACTIVITY

Concentration of Stabilizer =  $5.7 \times 10^{-3}$  moles/100 g. PVC-A

Sample	Temp. <sup>O</sup> C.	d HCl/dt x 10 <sup>8</sup> moles/g./sec.	к х 10 <sup>5</sup> sec. <sup>-1</sup>	$\theta = \frac{K_0 - K_s}{K_0}$	A400/moles of HCl x 10 <sup>-4</sup> Evolved	
Pure PVC-A	238	447.0	11.4	-	1.7	
Pure PVC-A + DBTDA	243	Initial 34.0 Final	1.0	0.94	1.7	
		295.0	10.1	0.42		
Pure PVC-A + DBTDL	239	Initial 50.4 Final 250.0	1.6 9.7	0.86 0.147	1.4	
Pure PVC-A + DBTM	243	22.6	0.60	0.96	1.7	

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DBTDA - Dibutyltin Diacetate ; DBTDL - Dibutyltin Dilaurate ; DBTM - Dibutyltin Maleate <sup>1400</sup> - The data was obtained from a separate experiment. This will be discussed under "Spectral Changes".

#### VI-5-3-i U.V.-Visible Spectral Changes

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Fig. VI-5 shows the plot of absorption at 400 mµ ( $A_{400}$ ), which wavelength is the absorption for about 5 conjugated double bonds<sup>(14)</sup>, with the time of heating at 160 ± 5°C. This figure reveals the fact that the increase of absorption at 400 mµ in the initial phase of degradation, is in the following order:

Acetate > Laurate > Maleate

Figure VI-6, shows the plot of HCl evolution vs. absorption at 400 mµ. It is interesting to note that the slopes of the lines are the same in every case. This means that the number of five double bond sequences produced per mole of HCl is the same. The stabilizer, only increases the time for the evolution of HCl and formation of double bonds.

### VI-5-3-ii Infrared Spectral Change with Stabilizers

The infrared spectra of PVC film containing organotin stabilizer (dibutyltin diacetate, dibutyltin dilaurate and dibutyltin maleate) were different from the spectra of pure PVC film in the 1500 cm<sup>-1</sup> to 1820 cm<sup>-1</sup> region. The bands in this region were attributed to the carboxyl group of the ester. On heating, only this region was affected. Therefore, in the present study, only this region 1500 cm<sup>-1</sup> to 1820 cm<sup>-1</sup> was studied.

The infrared spectra (1500  $\text{cm}^{-1}$  to 1820  $\text{cm}^{-1}$ 

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### FIGURE VI-5

THE EFFECT OF ORGANOTIN STABILIZER WITH DIFFERENT Y GROUPS ON ABSORPTION AT 400 MU WITH TIME OF HEATING.

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SAMPLE: PVC-A; TEMPERATURE:  $160 \pm 5^{\circ}C$ . ATMOSPHERE: NITROGEN, CONCENTRATION OF STABILIZER: 5.7 x  $10^{-3}$  MOLES/100 G.PVC-A

(O) PURE PVC-A ;

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- (X) PVC-A + DIBUTYLTIN DILAURATE
- ( $\Delta$ ) PVC-A + DIBUTYLTIN DIACETATE
- ( ) PVC-A + DIBUTYLTIN MALEATE



TIME, HRS.

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#### FIGURE VI-6

THE EFFECT OF ORGANOTIN STABILIZER WITH DIFFERENT Y GROUPS ON THE ABSORPTION AT 400 MML VS. HCl EVOLUTION.

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SAMPLE: PVC-A ; TEMPERATURE: 160 ± 5°C.

ATMOSPHERE: NITROGEN,

CONCENTRATION OF STABILIZER: 5.7 x 10<sup>-3</sup> MOLES/100 G.PVC-A.

(O) PURE PVC-A ;

()

- (X) PVC-A + DIBUTYLTIN DILAURATE
- ( $\Delta$ ) PVC-A + DIBUTYLTIN DIACETATE
- ( ) PVC-A + DIBUTYLTIN MALEATE



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region) of stabilized PVC film with dibutyltin diacetate, dibutyltin dilaurate and dibutyltin maleate, before and after heating are given in Fig. VI-7, A, B, and C, respectively.

In the case of PVC film stabilized with dibutyltin diacetate and dibutyltin dilaurate, the extra bands recorded in the  $1500 \text{ cm}^{-1}$  to  $1820 \text{ cm}^{-1}$  region, almost disappeared on heating, as is shown in Fig. VI-7, A and B. However, when dibutyltin maleate was used as a stabilizer, a broad band at 1700 to 1750 cm<sup>-1</sup> remained after heating. This behaviour of Dibutyltin maleate in the I.R. spectral change will be discussed in detail below.

VI-6

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#### DISCUSSION

Kenyon<sup>(8)</sup> in 1953, studied the photostabilizing action of dibutyltin diacetate, using a butyl group labelled with <sup>14</sup>C. He found an increase in the retained  $\beta$  activity in PVC with the time of irradiation, while with the <sup>14</sup>C. labelled -COOH in the acetate group this behaviour was not observed. He concluded that in the stabilizing action, only the butyl group took part and that it acted as follows:

$$(C_4H_9)_2S_n(OCOCH_3)_2 + R_2 \longrightarrow R_2C_4H_9 + C_4H_9Sn(OCOCH_3)_2$$
  
(VI-1)

where R<sub>2</sub> is a macroradical produced during degradation

- 170 -

### FIGURE VI-7

THE EFFECT OF ORGANOTIN STABILIZER ON INFRA-RED SPECTRAL CHANGE.

SAMPLE: PVC-A ; TEMPERATURE:  $160 \pm 5^{\circ}$ C. CONCENTRATION OF STABILIZER: 5.7 x  $10^{-3}$  MOLES/100 G.PVC-A

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# FIGURE VI-7A

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# THE EFFECT OF DIBUTYLTIN DIACETATE

()	BEFORE HEATING
()	AFTER HEATING

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# FIGURE VI-7B

# THE EFFECT OF DIBUTYLTIN DILAURATE

()	BEFORE HEATING
()	AFTER HEATING

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# FIGURE VI-7C

### THE EFFECT OF DIBUTYLTIN MALEATE

()	BEFORE HEATING
()	AFTER HEATING

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# FIGURE VI-7C

# THE EFFECT OF DIBUTYLTIN MALEATE

()	BEFORE HEATING
()	AFTER HEATING

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FREQUENCY ( $Cm^{-1}$ )

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Frye and Horst<sup>(1)</sup>, however, postulated that

- 172 -

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of PVC. Frye and Horst', however, postulated that polyvinyl chloride stabilization resulted from the replacement of labile chlorine atoms by the Y group of the stabilizer  $(C_4H_9)_xSnY_{4-x}$ . In spite of all this work, the mechanism by which organotins are acting as a stabilizer is still unclear.

The results (Table VI-1) with the organotin stabilizers having different numbers of butyl groups, that is dibutyltin dilaurate, tributyltin laurate, and tetrabutyltin, show that butyl groups exhibit stabilizing activity in the following order:

 $(C_4H_9)_4 \ge (C_4H_9)_3 > (C_4H_9)_2$ 

This order of decreasing stabilizing efficiency and lowering of  $\frac{dSpin}{dt}$  suggests that the butyl groups act as radical scavengers. Radicals generated by the cleavage of C-Sn bond, in the manner suggested by Kenyon<sup>(8)</sup> would be expected to be the active species. The rate of C-Sn bond cleavage, and thereby the rate of radical generation, is a function of the type of alkyl groups attached to the tin. Phenyl-Sn bonds are more easily cleaved than CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>-Sn<sup>(9)</sup>. The (PhCH<sub>2</sub>)<sub>4</sub>Sn was found to yield the PhCH<sub>2</sub> radical on heating in the same manner that tetraethyl lead <sup>(10)</sup> released C<sub>2</sub>H<sub>5</sub> radical. Thus, it is clear that on heating, a cleavage of the Sn-C bond takes place yield ing butyl radicals which react with the macroradical R<sub>2</sub> produced in PVC during degradation.

$$(C_{4}H_{9})_{2}S_{n}(OCOC_{11}H_{23})_{2} + 2R_{2} \longrightarrow 2C_{4}H_{9}R_{2} + S_{n}(OCOC_{11}H_{23})_{2}$$

$$(VI-2)$$

In this respect, we agree with the Kenyon mechanism<sup>(8)</sup>. Frye and Horst's mechanisms<sup>(1)</sup> of replacing labile chlorine by Y group of tin stabilizer is, however, a doubtful thesis. If their postulation is correct, then the action of tetrabutyltin stabilizer, where the Y group is absent, would be inexplicable. In addition to this, it is mentioned by them that compounds of the formula  $S_{1Y_4}$ , where x is zero, exert a deleterious effect on PVC's thermal stabilizer. This observation also cannot be explained by their mechanism. Now, let us see the effect of different Y groups on the scavenging action of butyl group.

The results from Table VI-2 for the HCl evolution with dibutyltin diacetate, dilaurate and maleate compound, and from the simultaneous spin generation curve, shown in Appendix Fig. AIII-9, which is a qualitative estimation, show that the nature of the Y group affects the cleavage of  $S_n$ -C bond in  $C_4H_9$ -Sn. Thus, we propose that organotin acts as a stabilizer by the following mechanism:

 $(C_{4}H_{9})_{2}S_{n}(OCC_{11}H_{23})_{2} + 2R_{2} + 2HC1$ (y),  $2C_{4}H_{9}R_{2} + SnCl_{2} + 2C_{11}H_{23}COOH$ 

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(2YH)

(VI-3)

The acid YH, produced in the above mechanism, on heating can act in two ways. If it is a monocarboxylic fatty acid, the chances of decomposing into  $CO_2$  and hydrocarbons are high<sup>(11)</sup>. This would explain the observations in the Infra-red spectra on PVC stabilized with dibutyltin dilaurate and dibutyltin diacetate. Before heating the sample, stabilized with these materials, absorption bands in 1500 cm<sup>-1</sup> to 1820 cm<sup>-1</sup> region of IR spectra were obtained. These disappeared on heating. This behaviour may be due either to the decomposition of HY acid or to its volatilization.

Maleic acid, a dicarboxylic acid, obtained by the heating of PVC film stabilized with dibutyltin maleate from the above reaction, yields maleic anhydride at elevated temperatures.



In this case, after heating the maleate stabilized PVC, a band in the region of 1500 cm<sup>-1</sup> to 1820 cm<sup>-1</sup> was retained. This shows the presence of -C- group in the degraded product. Both the dibutyltin maleate and the maleic anhydride can react with polyenes present in the degraded PVC by a Diels Alder reaction or with the active radicals.

Diels Alder Reaction



Reaction with active Radicals: -



The results of such reactions will be to diminish the extent of colour formation, by breaking up the length of the conjugated polyene sequences and a lowering in the rate of decomposition, through scavenging of active radicals. The diminution in the colour strongly suggests the presence of the first reaction (VI-5), while the second (VI-6) is proposed on the basis of the diminution in the rate of HCl evolution.

Thus, we conclude that in the stabilization of

PVC by organotin compounds

1) The cleavage of C-Sn bond takes place and  $C_4H_9$  radicals, produced in this way, couple with  $R_2$  radicals terminating a chain.

2) The cleavage of C-Sn bond depends on the nature of the Y group attached to the Sn atom by Sn-O bonding.

3) The acid moitie can further stabilize PVC, depending on the nature of Y group (reference Maleic ester).

#### V-7 SUMMARY AND CONCLUSIONS

In this Chapter, we have studied the mechanism of stabilization of PVC by organotin compounds of structure  $R_x SnY_{4-x}$ .

In experiments involving a series of compounds with different numbers of butyl groups, dibutyltin dilaurate (x=2), tributyltin laurate (x=3) and tetrabutyltin (x=4), stabilizing activity is in the following order

 $(C_4H_9)_4 \ge (C_4H_9)_3 \ge (C_4H_9)_2$ 

in other words, the rate of HCl evolution is in the following order

 $(C_4H_9)_4 \leq (C_4H_9)_3 < (C_4H_9)_2$ 

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The rates of spin generation were in the same order as that for  $\frac{dHCl}{dt}$ .

In experiments using compounds having different Y groups, acetate, laurate and maleate, it was shown that the maleate is a much better stabilizer than the other two compounds.

The Infra-red spectral change with these stabilizers show that after degradation, only compound containing maleate stabilizer retained the -C- group.

On the basis of these results, a mechanism for the stabilization of PVC, by organotin compounds, has been proposed.

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- 1. A.H. Frye, R.W. Horst, and M.A. Paliobagis, J. Polymer Sci., A2, 1765, 1785, 1801 (1964)
  - 2. Stareniye i Stabilizatsiya polimerov. (Ageing and Stabilization of Polymers), Izd. Nauka. 166,(1964).
  - 3. Z.V. Popova and D.M. Yanovskii, Zh. prikl. Khim, <u>34</u>, 1324 (1961).
- 4. A.L. Scarborough, W.L. Kellner and P.W. Rizzo, Mod. Plastics, 29, #9, 111 (1952).
- 5. K. Thinius, Chem. Tech. Bertin, 4, 81 (1952).
- 6. A. Rosenberg, Kunststoffe, <u>41</u>, 41 (1952).
- 7. G.P. Mack, Kunststoffe, 43, 94 (1953)
- 8. A.S. Kenyon, N.B.S. Circ., 525, 81 (1953).
- 9. "Die Organische Chemie des Zinns", by W.P. Neumann, 1967, Ferdinand Enke Verlag, Stuttgart, p.31.
- 10. Paneth and Hofeditz, Ber., 62, 1335 (1929); Paneth and Lautsch, Ber., 64B, 2702 (1931); J. Chem. Soc., 380 (1935).
- 11. J.D. Roberts and M.C. Caserio, "Basic Principles of Organic Chemistry" (1965), W.A. Denjamin, Inc., p. 551.

### CHAPTER VII

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### CONTRIBUTIONS TO ORIGINAL KNOWLEDGE AND

SUGGESTIONS FOR FURTHER WORK

#### VII-1 CONTRIBUTIONS TO ORIGINAL KNOWLEDGE

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The important findings of this investigation are summarized at the conclusion of each Chapter of this thesis, and are briefly listed below.

A new technique, simultaneous measurement of HCl evolution and spin generation during thermal degradation has been utilized to study the decomposition of polyvinyl chloride. The results lead to the following conclusions:

- The thermal degradation of PVC is a radical chain process for which the rate and activation energy for spin generation are associated with the initiation step.
- 2) A mechanism for the degradation is proposed. It is based upon a three-step reaction scheme, involving initiation, propagation and termination. The initiation step consists of the cleavage of a C-Cl bond. The Cl· radical produced in this step abstracts a hydrogen to generate an "active" radical which takes part in a two-step propagation reaction. The chain is terminated either by the coupling of two radicals or by the abstraction of a

- 179 -

chloromethylenic hydrogen. The calculation of the activation energy for the termination step (29 Kcal/mole) suggests that the termination step is diffusion controlled. The kinetic solution obtained from the proposed mechanism reveals that the dehydrochlorination should be a first order reaction. This is what was found experimentally.

- 3) The structural irregularities, tertiary hydrogen and tertiary chlorine atoms present in the polymer chain increase the rates of HCl evolution and spin generation. Tertiary hydrogens have no effect on the overall activation energy,  $E_{HCl}$  or on the activation energy for spin generation,  $E_{spin}$ . Tertiary chlorine atoms, however, reduce both  $E_{HCl}$ and  $E_{spin}$ .
- 4) The presence of an oxygen atmosphere during degradation increases the rates of HCl evolution and spin generation. A different kind of radical, a peroxy, was obtained in the presence of oxygen. On the basis of these findings, a mechanism for the role of oxygen on the degradation of PVC is proposed.
- 5) The pre-irradiation of PVC sample by U.V. rays facilitates the initiation step in the thermal decomposition reaction.

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On the basis of the findings, the mechanism by which the stabilization of PVC by organotin

following:

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(i) In the stabilization of PVC by compounds of the type  $R_x SnY_{(4-x)}$ , where R is connected to Sn atom by the C-Sn bond, the cleavage of the C-Sn bonds take place, and the R· radical produced couple with  $R_2$ · radicals (created during the degradation) terminating a chain.

(ii) The cleavage of C-Sn bond is dependent upon the nature of the Y group attached to the Sn atom.

(iii) The inclusion of dienophiles, e.g., maleic acid salts, among the Y groups, results in further stabilization and colour diminution by radical coupling and Diels Alder reactions, respectively.

#### VII-2 SUGGESTIONS FOR FURTHER WORK

 The technique of simultaneous measurements of HCl evolution and spin generation should be employed to study the photodecomposition of PVC. In this case, the sample should be irradiated during

compounds occurs, is rationalized to be the

the residence of the polymer inside the cavity of the E.S.R. instrument.

2) Further work should be performed on the PVC samples having structural irregularities not included in the present work. Among these are unsaturation, head-to-head structure and carbonyl groups, etc.

3) Further work should be undertaken, using stabilizers of different structures. Among these are the Pb, Ba and Cd salts of organic acids.

4) The technique of simultaneous measurements of HCl evolution and spin generation, used for PVC in the present work, should be employed to study the degradation of other polymers, e.g., polyvinylidene chloride, polyvinylacetate, etc.

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### APPENDICES

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#### APPENDIX I

MEASUREMENT OF NUMBER AVERAGE MOLECULAR WEIGHTS

BY HIGH SPEED MEMBRANE OSMOMETRY

In the following pages data and calculations for the number average molecular weights of PVC samples are given.

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## AI-1 DATA SHEET - MEMBRANE OSMOMETER



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AI-2 DATA SHEET - MEMBRANE OSMOMETER

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AI-3 DATA SHEET - MEMBRANE OSMOMETER

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AI-4 DATA SHEET - MEMBRANE OSMOMETER

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DATA SHEET - MEMBRANE OSMOMETER AI-5

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# AI.6 DATA SHEET - MEMBRANE OSMOMETER

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# APPENDIX II

# AII-1 CALCULATION FOR THE KINETIC SOLUTION

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The following reaction scheme is proposed in Chapter IV.

$$\frac{\text{Initiation}}{\text{-CH}_2\text{-CHCl-CH}_2\text{-CHCl-}} \xrightarrow{k_1} \text{-CH}_2\text{-CH-CH}_2\text{-CHCl-} + \text{Cl.}$$

$$(R_1 \cdot) \qquad (IV-4)$$

$$R_1 \cdot \text{+-CH}_2\text{-CHCl-CH}_2\text{-CHCl-} \xrightarrow{k_2} R_1\text{-H+-CH-CHCl-CH}_2\text{-CHCl-}$$

$$(R_2 \cdot) \qquad (IV-5)$$

$$\begin{array}{c} \cdot \\ -\text{CH-CHCl-CH}_2 - \text{CHCl-} & \xrightarrow{k_4} & -\text{CH=CH-CH}_2 - \text{CHCl-+Cl} \\ \\ (\text{R}_2 \cdot) & (\text{IV-7}) \end{array}$$

$$\frac{\text{Termination}}{\text{Cl} \cdot + R_2} \xrightarrow{k_5} R_2 \text{Cl} \qquad (IV-8)$$

$$\text{Cl} \cdot + -\text{CH}_2 - \text{CHCl} - \text{CH}_2 - \text{CHCl} - \xrightarrow{k_6} \text{HCl} + -\text{CH}_2 - \text{CCl} - \text{CH}_2 - \text{CHCl}$$

$$(R_1^{\dagger}.) \qquad (IV-9)$$

### The kinetic solution is as follows:

The "steady state" condition for a radical species is

$$\frac{d [Radical]}{dt} = - \frac{d [Radical]}{dt}$$
(AII-1)

In the following Section, this condition is applied for the radicals  $R_1 \cdot R_2 \cdot$  and Cl.

For  $[R_1 \cdot ]$ 

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 $\left( \begin{array}{c} \\ \end{array} \right)$ 

$$\frac{d[R_1 \cdot]}{dt} = \frac{d[R_1 \cdot]}{dt}$$

$$k_1[C] = k_2[R_1 \cdot][C] \qquad (AII-2)$$

where [C] is the concentration of monomer unit in polymer.

For [R<sub>2</sub>·]

$$\frac{d[R_2^{\cdot}]}{dt} = \frac{d[R_2^{\cdot}]}{dt}$$

or

$$k_{2}[R_{1}^{-}][C] + k_{3}[C1^{-}][C] = k_{4}[R_{2}^{-}] + k_{5}[C1^{-}][R_{2}^{-}]$$
(AII-3)

Substituting from (AII-2), (AII-3) becomes

$$k_1[C]+k_3[Cl\cdot][C] = k_4[R_2\cdot]+k_5[Cl\cdot][R_2\cdot]$$
 (AII-4)

or

$$\begin{bmatrix} R_{2} \cdot ]_{\pm} & \frac{k_{1}[C] + k_{3}[C1 \cdot ][C]}{k_{4} + K_{5}[C1 \cdot ]}$$
(AII-5)

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The steady state concentration for [Cl·] :

$$k_{1}[C]+k_{4}[R_{2}^{\cdot}] = k_{3}[Cl^{\cdot}][C]+k_{5}[Cl^{\cdot}][R_{2}^{\cdot}]+k_{6}[Cl^{\cdot}][C]$$
(AII-6)

Substituting  $[R_2 \cdot]$  from (AII-5), (AII-6) becomes  $k_1[C] + \frac{k_1k_4[C] + k_3k_4[Cl \cdot ][C]}{k_4 + k_5[Cl \cdot ]} = k_3[Cl \cdot ][C] k_6[Cl \cdot ][C] + \frac{k_1k_5[Cl \cdot ][C] + k_3k_5[Cl \cdot ]^2[C]}{k_4 + k_5[Cl \cdot ]} + \frac{k_1k_5[Cl \cdot ][C] + k_3k_5[Cl \cdot ]^2[C]}{k_4 + k_5[Cl \cdot ]}$ (AII-7)

Multiplying this equation by  $(k_4 + k_5[Cl \cdot ])$ , (AII-7) becomes;

$$2k_{1}k_{4}[C]+k_{1}k_{5}[Cl\cdot][C]+k_{3}k_{4}[Cl\cdot][C]$$

$$=k_{3}k_{4}[Cl\cdot][C]+k_{3}k_{5}[Cl\cdot]^{2}[C]$$

$$+k_{4}k_{6}[Cl\cdot][C]+k_{5}k_{6}[Cl\cdot]^{2}[C]+k_{1}k_{5}[Cl\cdot][C]$$
or 
$$[2k_{3}k_{5}+k_{5}k_{6}][Cl\cdot]^{2}+k_{4}k_{6}[Cl\cdot]-2k_{1}k_{4} = 0$$
(AII-8)

This equation (AII-8) is used in Chapter IV as (IV-17).

AII-2 CALCULATION OF KINETIC CHAIN LENGTH, V

Equation (AII-6) can be written as

$$[c1 \cdot ] = \frac{k_1[c] + k_4[R_2 \cdot ]}{k_3[c] + k_5[R_2 \cdot ] + k_6[c]}$$

(AII-9)

Substituting [Cl·] from (AII-9) in (AII-4),

we get:

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Left-hand side of equation (AII-4)

$$k_1^{[C]+k_3^{[C]} \times \frac{k_1^{[C]+k_4^{[R_2^{}]}}}{k_3^{[C]+k_5^{[R_2^{}}]+k_6^{[C]}}}}$$

or 
$$\frac{2k_{1}k_{3}[C]^{2}+k_{1}k_{5}[R_{2}^{\circ}][C]+k_{1}k_{6}[C]^{2}+k_{3}k_{4}[C][R_{2}^{\circ}]}{k_{3}[C]+k_{5}[R_{2}^{\circ}]+k_{6}[C]}$$

(AII-10)

and right hand side of (AII-4)

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or 
$$\frac{k_{3}k_{4}[R_{2}^{\circ}]+k_{5}[R_{2}^{\circ}] \times \frac{k_{1}[C]+k_{4}[R_{2}^{\circ}]}{k_{3}[C]+k_{5}[R_{2}^{\circ}]+k_{6}[C]}}{k_{3}[C]+k_{4}k_{5}[R_{2}^{\circ}]^{2}+k_{4}k_{6}[R_{2}^{\circ}][C]+k_{1}k_{5}[R_{2}^{\circ}][C]}{k_{3}[C]+k_{5}[R_{2}^{\circ}]+k_{6}[C]}$$

(AII-11)

Equating (AII-10) and (AII-11), we get  

$$2k_1k_3[C]^2 + k_1k_6[C]^2 = 2k_4k_5[R_2^2]^2 + k_4k_6[R_2^2][C]$$
(AII-12)

Assuming  $k_4^{k_6}$  a very small number and neglecting it (Section IV-12) in above, (AII-12) becomes

$$[R_2^{\cdot}] = \left[\frac{2k_1k_3 + k_1k_6}{2k_4k_5}\right]^{\frac{1}{2}} [C] \qquad (AII-13)$$

Substituting this in equation (IV-31) which is

$$v = \frac{k_3[C]}{k_5[R_2 \cdot ] + k_6[C]}$$
(IV-13)

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$$v = \frac{k_{3}^{[C]}}{k_{5} \left[\frac{2k_{1}k_{3}+k_{1}k_{6}}{2k_{4}k_{5}}\right]^{\frac{1}{2}} [C] + k_{6}^{[C]}}$$
(AII-14)

Solving equation (AII-14) and neglecting the term involving  $k_4 k_6$  we get  $v = \left[\frac{k_3 k_4}{k_1 k_5 + \frac{k_1 k_5 k_6}{2k_3}}\right]^{\frac{1}{2}}$ (AII-15)

or

$$v = \left[\frac{k_{3}k_{4}}{k_{1}k_{5}\left(1 + \frac{k_{6}}{2k_{3}}\right)}\right]^{\frac{1}{2}}$$
(AII-16)

which is equation (IV-33) in Chapter IV.

### APPENDIX III

Following are the figures, which have been referred to in Chapters IV and VI.

Figures AIII-1 to AIII-8, referred to on page 87 in Chapter IV.

Figure AIII-9, referred to on page 173.

in Chapter VI.

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# THERMAL DEHYDROCHLORINATION OF PVC-A IN NITROGEN ATMOSPHERE

(0) AT  $215^{\circ}$ C., ( $\Delta$ ) AT  $233^{\circ}$ C.

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SPIN GENERATION WITH TIME OF HEATING SAMPLE PVC-A IN NITROGEN ATMOSPHERE (O) AT  $215^{\circ}$ C., ( $\Delta$ ) AT  $233^{\circ}$ C.

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# THERMAL DEHYDROCHLORINATION OF PVC-B IN NITROGEN ATMOSPHERE

(()) AT  $215^{\circ}$ C., (0) AT  $233^{\circ}$ C. ( $\Delta$ ) AT  $243^{\circ}$ C.

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SPIN GENERATION WITH TIME OF HEATING SAMPLE PVC-B IN NITROGEN ATMOSPHERE.

( $\Box$ ) AT 215°C., (0) AT 233°C. ( $\Delta$ ) AT 243°C., REFERRED TO RIGHT-HAND AXIS.

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## THERMAL DEHYDROCHLORINATION OF PVC-C IN NITROGEN ATMOSPHERE

(0) AT 188.5°C., ( $\Delta$ ) AT 206°C.

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TIME, MIN.

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SPIN GENERATION WITH TIME OF HEATING SAMPLE PVC-C, IN NITROGEN ATMOSPHERE.

(0) AT 188.5°C., ( $\Delta$ ) AT 206°C.

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# THERMAL DEHYDROCHLORINATION OF PVC-D IN

NITROGEN ATMOSPHERE

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(0) AT 188.5°C., ( $\Delta$ ) AT 206°C. ( $\Box$ ) AT 215°C.

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SPIN GENERATION WITH TIME OF HEATING SAMPLE PVC-D, IN NITROGEN ATMOSPHERE.

(0) AT 188.5<sup>o</sup>C., (Δ) AT 206<sup>o</sup>C.
 (□) AT 215<sup>o</sup>C.

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TIME, MIN.

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EFFECT OF ORGANOTIN STABILIZERS WITH DIFFERENT Y GROUPS IN STRUCTURE  $R_x SnY_{4-x}$ , ON THE RATES OF SPIN GENERATION. SAMPLE PVC-A ; TEMPERATURE: 242 ± 1°C. CONCENTRATION OF STABILIZER: 5.7 x 10<sup>-3</sup> MOLES/100G.PVC-A ATMOSPHERE: NITROGEN, (---X---) PURE PVC-A; (O) PVC-A + DIBUTYLTIN DILAURATE

( $\Delta$ ) PVC-A + DIBUTYL DIACETATE

( ) PVC-A + DIBUTYLTIN MALEATE

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## APPENDIX IV

## DATA FOR THE FIGURES

In the following pages, data for the main figures, used in the present thesis, are given.

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## A IV-1 DATA FOR FIGURE IV-8

HCl evolution	from PVC	Samples with	a time of
h	eating at	224 <sup>0</sup> C.	

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PVC-A		PVC-B		PVC-C		PVC-D	
Time,Min.	HClx10 <sup>4</sup> moles/g.	Time,Min.	$HClx10^4$ moles/g.	Time,Min.	$HClx10^4$ moles/g.	Time,Min.	HClx10 <sup>4</sup> moles/g.
21	0.9	20	0.12	3	1	5.0	2.0
40	7.7	30	0.7	7	18.00	10	19.7
50	17.3	53	6.8	12	35.0	17	39.5
75	50.4	70	9.5	34	42.7	25	55.5
80	54.1	85	15.6	70	48.00	30	61.0
90	64.2	115	27.1	<u>,</u> 80	48.0	78	78.3
100	71.0	135	34.0				
121	76.5	140	35.3				
133	78.6						

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## A IV-2 DATA FOR FIGURE IV-9

of heating at 2240C.								
PV	C-A	PVC-B		PVC-C		PVC-D		
Time,Min.	Spin/gxl0 <sup>-15</sup>	Time,Min.	Spin/gxl0 <sup>-15</sup>	Time,Min.	Spin/gxl0 <sup>-15</sup>	Time,Min.	$\frac{15}{/g}$	
40	7.2	65 90	3.6 8.2	4	32.8 49.3	3	24.0 39.0	
60	20.7	110	10.0	14	54.0	13	47.0	
80	40.5	120	12.8	19	55.10	18	56.0	
100	53.0	130	13.7	34	57.5	28	57.0	
,						38	56.0	
120	56	140	15.1	44	59.8			
						48	56.4	
				54	62.2			
						63	56.4	
				64	64.5			
				74	71.5			
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# Spin generation from PVC Samples with time of heating at 2240C.

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### A IV-3 DATA FOR FIGURE V-1

The	effect	of	oxygen	on	thermal	. dehyo	droch.	lorination
		C	of PVC	-A.	Temper	ature	1969	<sup>5</sup> C.

In Nitrogen		In Oxyg	en	When O was Introduced During Degradation in Nitrogen		
Time,Min.	HClx10 <sup>4</sup> moles/g.	Time,Min.	HClx10 <sup>4</sup> moles/g.	Time,Min	HClx10 <sup>4</sup> moles/g.	
40 78 128 165 206 212 240 285 296 315 355	.5 1.1 3.0 5.8 11.7 12.5 18.7 29.7 32.0 37.5 47.2	144 150 162 177 192 218 240 260	1.0 2.20 5.6 11.25 17.86 28.3 35.7 40.0	<u>In Nitrogen</u> 45 63 93 118 145 (Oxygen at 180 220 240 262.5 282 296 320 333	.6 1.06 1.7 2.2 2.8 175 min.) 4.0 4.4 11.2 22.3 35.5 44.7 62.9 70.3	

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#### A IV-4 DATA FOR FIGURE V-2

The effect of oxygen on spin generation by thermal dechlorination of PVC-A at 196° C.

In Nitr	ogen	In Oxy	rgen	When O <sub>2</sub> was Introduced During Degradation in Nitrogen		
Time,Min.	Spinxl0 <sup>-15</sup>	Time,Min.	Spinxl0 <sup>-15</sup> /g.PVC.	Time,Min.	Spinxl0 <sup>-15</sup> /g.PVC.	
	/ 9			In Nitrogen		
				55	1.00	
80	1.00	60	1.12	150	1.2	
175	1.5	100	4.2	Oxygen at 17	5 mins.	
215	1.94	120	6.4	200	1.4	
255	3.06	130	8.6	225	3.83	
295	4.08	140	11.6	240	6.05	
330	4.7	150	15.5	250	8.2	
340	5.3	155	17.8	260	12.2	
360	5.6	175	27.8	270	16.35	
300		180	31.2			
		185	34.7	280	21.3	
		190	38.2	300	34.60	
				320	46.0	
		200	44.17			
				330	53.9	

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#### A IV-5 DATA FOR FIGURE V-10

Effect of U.V. irradiation on thermal dehydrochlorination of PVC-A at 200°C. in Nitrogen Atmosphere

For O hr. pre- irradiated sample		For l hr. pre- irradiated sample		For 2 <sup>1</sup> / <sub>4</sub> hrs.pre- irradiated sample		For 3 hrs.pre- irradiated sample	
Time,Min. HC mc F	Clx10 <sup>4</sup> oles/g. PVC	Time,Min.	HClx10 <sup>4</sup> moles/g. PVC	Time,Min.	HClx10 <sup>4</sup> moles/g. PVC	Time,Min.	HClx10 <sup>4</sup> moles/g. PVC
90   130   210   1.   285   330   382   408   408   441   6   470	.52 .6 .5 .3 .1 .2 .1 .8 .7	15 35 97 135 165 212 240 270 300 332 375 425 480 540	.7 1.5 2.9 4.1 5.0 7.0 9.25 12.6 16.4 21.1 27.6 36.7 42.2 47 7	30 60 90 125 165 195 240 272 308 332 390 455 480 512	2.0 3.0 4.1 5.27 6.8 8.7 12.3 15.8 20.6 24.2 33.5 44.2 48.0 52.5	25 35 51 90 135 168 240 285 300 330	1.5 2.1 2.8 4.3 6.4 8.9 19.0 28.0 31.7 38.0

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#### A IV-6 DATA FOR FIGURE V-11

Effect of U.V. irradiation on spin generation by thermal dehydrochlorination of PVC at 200°C.

For O hr. pre- irradiated sample		For l hr. pre- irradiated sample		For 2 <sup>1</sup> / <sub>4</sub> hrs.pre- irradiated sample		For 3 hrs. pre- irradiated sample	
Time,Min.	Spinxl0 <sup>-15</sup> /g.PVC	Time,Min	.Spinxl0 <sup>-15</sup> /g.PVC	Time,Min	.Spinxl0 <sup>-15</sup> /g.PVC	Time,Min	Spinxl0 <sup>-15</sup> /g.PVC
375 420 455 520	2.36 3.07 3.54 4.25	0 90 135 175 240 310 385 420 450 510	2.9 4.4 5.8 6.6 8.1 8.8 10.3 11.74 12.45 13.25	0 30 60 90 140 190 215 235 285 330 350 375 420 480 510	3.9 7.1 8.1 8.4 9.8 10.4 11.7 12.4 13.7 15.6 16.4 17.7 20.8 24.8 27.5	0 30 60 90 130 160 190 230 240 270 290 300	4.85 8.5 9.9 11.5 12.4 13.3 14.5 17.0 18.19 20.6 23.0 23.65 26.7
				520	29.0	335	20.7

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#### A IV-7 DATA FOR FIGURE VI-1

Effect of organotin stabilizer with various number of x in the structure  $R SnY_{4-x}$ , on the rates of HCl evolution x at 238°C.

Pure PVC-A		PVC-A + I	(1) PVC-A + DBTDL		(2) PVC-A + TBTL		(3) PVC-A + TBT	
Time,Min.	HClx10 <sup>4</sup> /g.PVC	Time,Min.	HClx10 <sup>4</sup> /g.PVC	Time,Min.	HClx10 <sup>4</sup> /g.PVC	Time,Min	HC1x10 <sup>4</sup> /g.PVC	
20 30 40 50 <b>55</b> 60 80	3.2 23.4 47.2 53.7 62.1 69.0 72.1	20 30 40 60 80 100 120 140 150 160 175	1.7 4.6 6.6 11.4 16.6 22.7 30.16 48.2 67.8 77.0 82.0	20 41 61 81 102 121 141 161 182 202 221 246	1.3 5.3 9.2 14.6 19.7 23.9 29.0 33.0 36.7 41.3 45.1 53.0	20 40 46 87 100 130 151 170 196 210 240 255 270 305	1.5 5.3 10.1 15.0 17.8 27.2 31.6 36.0 41.4 45.4 53.6 55.5 61.6	

(1) DBTDL : Dibutyltin dilaurate.

(2) TBTL : Tributyltin Taurate

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#### A IV-8 DATA FOR FIGURE VI-2

Effect of organotin stabilizers with various numbers of x in the structure  $\underset{x}{\text{R}}_{4-x'}$  on the rates of spin generation

Pure PVC-A		PVC-A + DBTDL		PVC-A + TBT		PVC-A + TBTl	
Time,Min	.Spinxl0 <sup>-16</sup> /g.PVC	Time,Mir	.Spinxl0 <sup>-16</sup> /g.PVC	Time,Mi	n.Spinxl0 <sup>-16</sup> /g.PVC	Time Spin Min.	x10 <sup>-16</sup> /g.PVC
10 20 30 40 55 65	2.2 8.3 13.3 13.7 13.16 13.5	20 40 60 80 90 95 110 120 130 150 165	2.7 5.5 8.3 11.5 13.31 14.00 15.6 18.36 20.2 23.4 23.8	20 40 60 80 100 110 130 145 160 170 190 210 235 250	.9 2.5 4.3 6.0 8.06 9.39 9.75 11.5 12.36 12.77 13.8 13.6 13.6	20 40 60 81 100 120 141 166 176 220	2.0 4.5 6.8 9.2 11.00 12.8 14.6 14.97 15.3 15.43

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#### A IV-9 DATA FOR FIGURE VI-6

Effect of organotin stabilizers with different y groups on the rates of HCl evolution

Pure PVC-A		PVC-A + DBTDL		PVC-A + DBTDA		PVC-A + DBTM	
Time,Min.	HClx10 <sup>4</sup> moles/g. PVC	Time,Min.	HClx10 <sup>4</sup> moles/g. PVC	Time,Min.	HClx10 <sup>4</sup> moles/g. PVC	Time HCl ×10 <sup>4</sup> Min. Moles/g. PVC	
20 30 40 50 55 60 80	3.2 23.4 47.2 53.7 62.1 69.0 72.1	20 40 60 80 100 111 118 120 130 140 160 170	.8 2.6 5.0 7.50 10.61 14 20.1 30 60.9 71.4 77.0 77.9	30 50 70 90 110 117 130 140 150 165 192 215 240	2.9 6.8 11.0 16.0 20.0 24.3 42.5 58.3 69 77.2 81.5 23.19 84.8	40 60 80 100 120 140 160 180 200 220 240 280 300 336 360	1.1 2.6 4.7 6.8 8.8 11.6 14.5 17.2 20.00 23.0 25.00 28.7 30.6 33.4 35.5

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#### A IV-10 DATA FOR FIGURE A III-1

AT 2	15 <sup>0</sup> c.	AT 233 <sup>0</sup> C.			
Time, Min. HClx10 <sup>4</sup> moles/g.		Time, Min.	HClxl0 <sup>4</sup> moles/g.		
30	1.2	20	4.0		
45	3.5	30	19.5		
55	8.0				
60	11.4	40	43.2		
70	19.2				
90	37.7	50	63.6		
110	53.3				
130	65.5	60	76.0		
		68	81.0		
		73	83.0		
		85	85.4		
		104	87.6		

Thermal dehydrochlorination of PVC-A in nitrogen atmosphere.

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#### A IV-11 DATA FOR FIGURE A III-2

AT	215 <sup>0</sup> c.	AT 23	АТ 233 <sup>0</sup> С.			
Time, Min. Spin/gxl0 <sup>-15</sup>		Time, Min.	Spin/gxl0 <sup>-15</sup>			
· · · · · · · · · · · · · · · · · · ·						
55	5.0	15	11.6			
70	8.3	20	19.7			
85	12.5	30	50.6			
105	20.8	40	84.4			
125	29.2	50	103.7			
145	33.4	55	104.1			
165	34.2	65	107.0			
180	180 34.0		109.7			

# Spin generation with time of heating sample PVC-A in nitrogen atmosphere.

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#### A IV-12 DATA FOR FIGURE A III-3

# Thermal dehydrochlorination of PVC-B in nitrogen atmosphere.

AT 21	AT 215 <sup>0</sup> C.		<sup>9</sup> c.	АТ 243 <sup>0</sup> С.		
Time, Min.	HClxl0 <sup>4</sup> moles/g.	Time, Min.	HClx10 <sup>4</sup> moles/g.	Time,Min.	HClx10 <sup>4</sup> moles/g.	
60	1.2	16	3.0	10	6.2	
60	1.5	22	5.0	10	34 5	
100	3.35	22	0.0	10	54.5	
140	9.0	30	11.7	20	61.5	
180	17.0	35	18.7	25	76.5	
220	25.4	44	37.45	30	84.4	
260	33.0	54	59.3	35	89.0	
300	39.6	60	70.7	40 .	91.7	
360	43.6	65	03.8			
		75	94.1			
	,	85	99.6			
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### A IV-13 DATA FOR FIGURE A III-4

АТ 215 <sup>0</sup> С.		АТ 233 <sup>0</sup> С.		AT 243 <sup>0</sup> C.		
Time, Min.	Spin/gxl0 <sup>-15</sup>	Time,Min.	Spin/gxl0 <sup>-15</sup>	Time,Min.	Spin/gxl0 <sup>-16</sup>	
50	1.4	20	9.5	5	1.6	
100	2.1	30	14.6	10	5.7	
140	4.6	40	32.0	15	15.4	
180	7.8	50	49.6	20	22.16	
220	10.2	60	61.10	30	26.0	
260	13.0	70	64.0	40	27.3	
305	15.0	80	64.3	50	28.7	
355	16.7					
395	18.5					

Spin generation with time of heating sample PVC-B in nitrogen atmosphere.

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## A IV-14 DATA FOR FIGURES AIII-5 and -6

Thermal dehydrochlorination and spin generation of PVC-C in nitrogen atmosphere.

HCl Evolution AT 188.5°C. AT 206°C.			Spin Generation AT 188.5 <sup>0</sup> C.		AT 206 <sup>0</sup> C.		
Time,Min	HClx10 <sup>4</sup> moles/g.	Time,Min.	HClx10 <sup>4</sup> moles/g.	Time,Min.	HClx10 <sup>4</sup> moles/g.	Time,Min.	HClx10 $\frac{4}{1}$ moles/g.
		6	1.8	10	9.0	5	16
10	.97	10	16.3	20	17	10	48
20	7.8	15	31.0	30	23	15	63 70
31	15.4	20	40.6	40	28	35	71.5
41	21.7	25 30	46.0 49.3	50 60	30.6 33.0		
60	28.8	40	53.3				
70	35.0	50	55.7	80	37.75		
80	36.7	63	57.0	TOO	57.75		
100 125	41.0						· ·

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#### A IV-15 DATA FOR FIGURE A III-7

## Thermal dehydrochlorination of PVC-D in nitrogen atmosphere.

AT 188.5 <sup>0</sup> C.		AT 206	°c.	AT 215°C.		
Time,Min.	HClx10 <sup>4</sup> moles/g.	Time,Min.	HClx10 <sup>4</sup> moles/g.	Time,Min.	HClx10 <sup>4</sup> moles/g.	
10	4.0	10	4.6	7	2.1	
				10	10.3	
20	19.1	20	23.3	15	25	
		30	35.0	20	36.7	
. 30	31.6	35	44.0	25	46.7	
		40	51.0	30	54.3	
40	42.5	55	66.0	35	61.2	
50	51.8	75	81.6	45	71.0	
60	61.0	95	92.7	55	80.5	
80	75	115	103.4	60	83.7	
95	85			75	90.4	
125	102.4			85	93.8	
150	104.2			98	97.3	

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# A IV-16 DATA FOR FIGURE A III-8

۵۳ 188.5 <sup>0</sup> C.		AT 2	206 <sup>0</sup> C.	AT 215 <sup>0</sup> C.		
Time,Min.	Spinxl0 <sup>-15</sup> /g.PVC.	Time,Min.	Spinxl0 <sup>-15</sup> /g.PVC	Time,Min.	Spinxl0 <sup>-15</sup> /g.PVC	
5 15	2.1 9.08	5 10	5.8 19.6	5 10	13 33	
25	13.20	20	34.45	20	52	
35	15.1	30	43.0			
45	16.6	35	46.3	30	65	
55	17.7	40 50	40.7	35	. 73	
65	18.6	60	60.7	40	80	
75	20.12	75	70.00	50	88	
90	21.8	85	75.0	55	90.5	
		90	80.1	60	92	
115	23.37	100	82.00	70	93	
155	25.5	110	83.6	80	92	

# Spin generation with time of heating sample PVC-A in nitrogen atmosphere.

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#### A IV-17 DATA FOR FIGURE A III-9

Buro BVC		With DBTDL		With DBTDA		With DBTM	
Time,	Spinxl0 <sup>-15</sup>	Time,Min.	Spinxl0 <sup>-15</sup>	Time,Min.	Spinxl0 <sup>-15</sup> /g. PVC	Time,Spin Min.	x10 <sup>-15</sup> /g. PVC
E	12.2	35	1.0	20	2.6	10 25	3.0 6.2
5	12.3	50	1.4	40	3.6	50	12.7
10	22.0 A7 A	70	1.7	60	5.6	75	18.0
20 T2	47.4	80	2.0	80	7.1	100	23.4
20	03.4	100	2.25	100	9.1	125	30.2
		120	2.5	120	10.3	150	35.0
		125	2.9	140	12.5	175	40.6
		140	3.46	161	19.5	200	42.7
		150	4.028	181	22.0	250	47.4
				201	23.8	280	50.7
				216	23.8	300 350 390	53.3 56.0 58.07

# Effect of organotin stabilizers with different y groups in structure $R_x SnY_{4-x}$ , on the rates of spin generation.

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