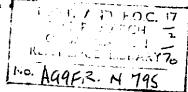# Fire Research Note
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EXPERIMENTAL AND THEORETICAL STUDIES OF THE
DEHYDROCHLORINATION OF PVC IN AIR AND NITROGEN

by

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SUMMARY

The release of hydrogen chloride from the thermal decomposition of a sample of a commercial rigid PVC has been studied in air and nitrogen between 200 and 300°C. It is shown that the dehydrochlorination can be represented by a 3/2 order decomposition with activation energies of 36.1 and 41.5 K cals. mole^{-1} in air and nitrogen respectively. The report explains how this kinetic data can be used to predict the total release of hydrogen chloride as a function of time from the decomposition of PVC during either isothermal conditions or non-linear temperature increments as in fires. A comparison is shown between the experimental and calculated release of hydrogen chloride during a temperature programmed experiment between 200 and 300°C.

KEY WORDS: Combustion products, hydrogen chloride, toxic gas, poly(vinyl-chloride)

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1. INTRODUCTION

a) General Introduction

An earlier report outlines a study, by gas chromatography and mass spectrometry, of the decomposition products of PVC in air and nitrogen between 300 and 550°C[1]. The release of hydrogen chloride was monitored during these experiments and found to be accompanied by the release of the many minor decomposition products, mainly aromatic and aliphatic hydrocarbons. In these studies, some attempts were made to use the dehydrochlorination data to formulate a general kinetic rate equation to represent dehydrochlorination. Unfortunately, even at 300°C, the rate of the evolution of hydrogen chloride in the laboratory experiments was too rapid to derive this kinetic relationship.

In this report the study of the dehydrochlorination of a commercial rigid PVC in air and nitrogen has been extended to a lower temperature range, namely 200 to 300°C. It is shown that, as suggested by Stromberg et al[2], the dehydrochlorination can be represented by a 3/2 order decomposition based upon the fraction of residual hydrogen chloride in the polymer. In nitrogen the relationship appears to be valid up to approximately 80 per cent of theoretical dehydrochlorination but in air the relationship is less accurate and extends to only 70 per cent of the theoretical.

Using this kinetic data it is shown that the release of hydrogen chloride with time may be calculated for non-linear temperature-time profiles as in fires. For this evaluation the temperature-time profile is subdivided into a series of time intervals and the extent of dehydrochlorination calculated from the kinetic data assuming a constant mean temperature over each interval. The method is demonstrated by monitoring the release of hydrogen chloride in a temperature programmed laboratory experiment and comparing the experimental and calculated dehydrochlorination curves.

Finally, it should be emphasized that this report is not designed to be a detailed kinetic analysis of the dehydrochlorination reaction. It is intended to be a practical introduction to dehydrochlorination and in particular to show how this kind of data can be used for estimating the release of hydrogen chloride solely from temperature measurements.

b)   The Dehydrochlorination of PVC

The mechanism of the dehydrochlorination of PVC has been outlined in a series of papers and in particular in a recent review by Geddes[3]. A summary of the mechanism was presented in an earlier report[1].

Kinetic studies of the rate of dehydrochlorination have been mainly concerned with relatively low levels of dehydrochlorination since this is the region of interest in the ageing, stability and general weathering properties of PVC.

In 1959, Stromberg[2] and his co-workers studied the dehydrochlorination in vacuum between 235 and 260°C and found the elimination to be a 3/2 order reaction over a wide range of dehydrochlorination given by:-

$$- \frac{dC}{dt} = k \ C^{3/2}$$

where   C   is the fraction of undegraded units in the polymer chain.

The authors further showed that this relationship was valid for three different types of PVC and quoted activation energies of 26, 30 and 32 K cals. mole^{-1} for PVC polymerised by azo-bis-isobutyronitrile, benzoyl peroxide and γ - radiation respectively.

Talamini and Pezzin[4] studied the dehydrochlorination of PVC in nitrogen and air over the temperature range 200 to 220°C and found that the initial rate of dehydrochlorination was inversely proportional to the molecular weight of the polymer. Oxygen gave a marked increase in the rate of evolution of hydrogen chloride and activation energies of 24 and 33 K cals. mole^{-1} were reported for the decompositions in air and nitrogen respectively.

2.   EXPERIMENTAL

a)   General Experimental

The essential features of the apparatus and details of the analytical procedures for monitoring the hydrogen chloride have been outlined in a recent report[1]. For convenience the main parts of the equipment relevant to the present studies are shown in Figure 1.

Samples of the PVC (30 mg) are decomposed in a small ceramic boat which is injected into the furnace by the influence of an external magnet on the steel plug P. During the decomposition, a flow of dry air or nitrogen (B.O.C. white spot grade) at 100 ml/min at 20°C is maintained through the furnace tube and

extracts the hydrogen chloride from the hot furnace zone. The heated gas analysis line to the chromatograph is closed for these experiments and the hydrogen chloride is diverted down the side arm S and bubbled through 20 ml of distilled water. The flow system is constructed entirely of borosilicate glass. The main exit tube from the furnace and part of the side arm S are maintained at 150°C with electrical heating tape to avoid absorption problems.

The hydrogen chloride released from the decomposition is monitored in situ by titrating with N/25 sodium hydroxide added from a burette. In practice during a dehydrochlorination experiment it was more convenient to add known amounts of sodium hydroxide and record the time taken to reach the end point rather than attempt an end point titration at known time intervals. Phenolphthalein (pH 8 to 10) was used as indicator in experiments with nitrogen carrier gas. In air this was replaced by dimethyl yellow (pH 3 to 4) to avoid possible problems from carbon dioxide. A test dehydrochlorination confirmed that in the nitrogen experiments the two indicators gave identical results.

The temperature of the decomposition furnace is stabilised with a modified temperature controller for operation up to 1000°C (temperature stability $\pm$ 2°C at 500°C). For convenience the furnace temperature is displayed on a 0 to 800°C direct reading meter.

In the furnace calibration experiments, the temperature of samples inside the ceramic boat were monitored by a thermocouple attached directly to a digital voltmeter. The fast response and 'hold readout' facilities of the instrument provided a convenient means of examining the rate of temperature increase of test samples injected into the furnace. For these experiments the 'hold readout' button was pressed at various time intervals after injection and the thermocouple potential recorded. In this way sample temperatures could be recorded every few seconds, if necessary, after injection.

b) Materials

The PVC used in the experiments of this report was cut as small cubes (3 to 4 mg each) from a rigid commercial sheet of the type used to study the behaviour of PVC in fires[5]. According to the manufacturers the PVC contained approximately 10 per cent of organic and inorganic additives by weight with a theoretical hydrogen chloride content of 50.6 per cent.

A total sample weight of 30.0 $\pm$ 1.0 mg was used in all dehydrochlorination experiments and the data corrected for a sample weight of 30.0 mg.

3. RESULTS

a) Furnace Calibration Experiments

Calibration experiments yielded the rate of temperature increase of samples injected into the furnace and the correlation of the furnace control temperature with the final equilibrium sample temperature. For these experiments small pieces of ceramic insulators (approximately 4 mg each) with a total weight of 30 mg were placed into the ceramic boat and a thermocouple (36 SWG) inserted into the hollow portion of the insulator near the centre of the boat. It was anticipated that the temperature behaviour of these ceramics would be comparable with that of the actual PVC samples. Temperature profiles for various furnace temperatures were recorded in this way using the digital voltmeter as outlined in the experimental section.

Figure 2 shows the temperature profiles of the ceramics at furnace temperatures of 245, 300, 400, 500 and 600°C in nitrogen flowing at 100 ml/min at 20°C. Approximately twenty points were obtained for each profile but these actual points have been omitted from the figure for convenience.

In each profile there is a distinct time required to bring the sample to the final equilibrium level. This time varies with furnace temperature and at 300°C a time of approximately six minutes is required. At 300°C the time for complete dehydrochlorination is of the order of seven minutes[1] and clearly kinetic measurements at temperatures above about 300°C are of little value.

As expected, in each profile of Figure 2 the final sample temperature is less than the furnace control temperatures and for calibration purposes the correlation between these temperatures from 200 to 600°C is shown in Figure 3*. For convenience the section between 200 and 300°C has been studied in more detail and is shown in Figure 4.

The gas temperatures inside the furnace were also monitored with the thermocouple during the calibration tests. In general these gas temperatures were very close to the final sample temperatures. For example at a furnace temperature of 500°C the final sample temperature was 485°C and the gas temperature 480°C.

b) The Dehydrochlorination of PVC in Nitrogen

Figure 5 shows the release of hydrogen chloride from 30 mg samples of the commercial PVC in nitrogen at furnace temperatures between 218 and 275°C (final sample temperatures 219 to 267°C) for periods up to 50 minutes. Hydrogen

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*Although calibration data above 300°C are not directly relevant to this report they are recorded here to assist current work on thermosetting resins.

chloride is plotted as the percentage of the theoretical amount available from this PVC.

In Figure 5, the induction period (i.e. the time between injection and the detection of hydrogen chloride) which includes the collection time lag and part of the sample heating time is quite distinct and is of the order of 2 to 3 minutes. The complete sample heating time (from Figure 2) is about 6 minutes at these temperatures and the assumption of a constant sample temperature during the majority of this dehydrochlorination study is justified.

According to the data of Stromberg and co-workers the dehydrochlorination may be represented as a 3/2 order decomposition based upon the concentration of residual hydrogen chloride in the polymer. For convenience, in this report the hydrogen chloride evolved will be expressed in all cases as a percentage of the theoretical amount available from the PVC.

Assume that after a time (t) the PVC has released a percentage (P) of the theoretical hydrogen chloride.

Then residual hydrogen chloride $= (100-P)$ $\quad\quad\quad\quad\quad\quad$ ..... (1)
and for a 3/2 order decomposition

$$\frac{-\,d(100-P)}{dt} = k\,(100-P)^{3/2} \quad\quad\quad ..... (2)$$

where k is the rate constant.
Equation (2) on integration yields

$$(100-P)^{-\frac{1}{2}} = (100)^{-\frac{1}{2}} + \tfrac{1}{2}kt$$

or

$$(100-P)^{-\frac{1}{2}} = 0.1 + \tfrac{1}{2}kt \quad\quad\quad\quad ..... (3)$$

Hence a graph of $(100-P)^{-\frac{1}{2}}$ against the time (t) should give a straight line of slope (k^1) where $k^1 = k/2$.

Figure 6 shows the dehydrochlorination data of Figure 5 plotted in this way. For convenience the $(100-P)^{-\frac{1}{2}}$ scale is also shown as a non-linear scale of (P). Temperatures given in the figure are final sample temperatures. As can be seen, a reasonable kinetic relationship for a 3/2 order decomposition* is valid up to about 80 per cent of theoretical dehydrochlorination. The straight lines for each decomposition temperature are drawn by eye.

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*The kinetic data was also plotted for a first and second order decomposition, namely by plots of $\log_{10}(100-P)$ and $(100-P)^{-1}$ versus time respectively. In each case a certain degree of linearity was found but the 3/2 order plot showed a more accurate linearity over a wider range of dehydrochlorination.

A summary of the decomposition temperatures and rate constants is shown in Table 1.

Table 1. Rate Constants for Dehydrochlorination in Nitrogen

Furnace Temperature ($^\circ$C)	Final Sample Temperature ($^\circ$C)	Slope of 3/2 order plot (k^1) (per cent$^{-\frac{1}{2}}$. min^{-1}.)	Rate Constant $k = 2k^1$ (per cent$^{-\frac{1}{2}}$. min^{-1})
275	267	1.05×10^{-2}	2.10×10^{-2}
264	256	5.37×10^{-3}	1.07×10^{-2}
250	243	2.03×10^{-3}	4.06×10^{-3}
238	232	7.63×10^{-4}	1.53×10^{-3}
230	224	4.60×10^{-4}	9.20×10^{-4}
225	219	2.20×10^{-4}	4.40×10^{-4}

c) The Dehydrochlorination of PVC in Air.

Figure 7 shows the release of hydrogen chloride from the decomposition of the PVC in a flow of air (100 ml/min) plotted again as percentage of the theoretical. Temperatures recorded in Figure 7 for each profile are final sample temperatures.

The equivalent data plotted for a 3/2 order decomposition (i.e. $(100-P)^{-\frac{1}{2}}$ versus time) is shown in Figure 8. As can be seen the 3/2 order relationship is less accurate than for the dehydrochlorination in nitrogen. The data was also plotted for a first and second order decomposition namely by plots of $\log_{10}$ (100-P) and $(100-P)^{-1}$ versus time respectively. As in the nitrogen experiments, some linearity was found for each of these relationships and even the plots in Figure 7 show some linearity up to 50 per cent of dehydrochlorination. The 3/2 order plot shown in Figure 8, although giving a distinct sigmoidal shape to the contours, did extend the linear range to the highest percentage of dehydrochlorination. In Figure 8 the straight lines for each decomposition temperature have been drawn by eye through most of the points up to 70 per cent of dehydrochlorination and the rate constants are summarised in Table 2.

Table 2. Rate Constants for Dehydrochlorination in Air

Furnace Temperature ($^\circ$C)	Final Sample Temperature ($^\circ$C)	Slope of 3/2 order plot (k^1) (per cent$^{-\frac{1}{2}}$. min^{-1}.)	Rate Constant $k = 2k^1$ (per cent$^{-\frac{1}{2}}$. min^{-1}.)
280	272	1.62×10^{-2}	3.24×10^{-2}
265	257	6.29×10^{-3}	1.26×10^{-2}
250	243	2.64×10^{-3}	5.28×10^{-3}
240	232	1.34×10^{-3}	2.68×10^{-3}
230	224	4.88×10^{-4}	9.76×10^{-4}
218	212	2.33×10^{-4}	4.66×10^{-4}

d) Arrhenius Plots for Dehydrochlorination in Nitrogen and Air

Since the dehydrochlorination in nitrogen and air can be regarded as a definite order of decomposition for a wide range of temperatures the data for the dehydrochlorination has been represented by Arrhenius equations namely that

$$k = A\, e^{-E/RT} \qquad \dots\dots (4)$$

where A is a pre-exponential constant, E the activation energy, R the gas constant and T the temperature in degrees absolute.

Equation (4) is often written as

$$\log_{10} k = \log_{10} A - \frac{E}{2.303\,RT} \qquad \dots\dots (5)$$

such that a plot of $\log_{10}$ k versus $1/T$ gives a straight line of slope $-E/2.303\,R$.

The data of Tables 1 and 2 calculated for Arrhenius plots are tabulated in Tables 3 and 4 and shown graphically in Figure 9. The straight lines through each set of points are drawn by eye and the equations of these lines and the corresponding activation energies are given below.

(i) Dehydrochlorination in Nitrogen

The slope of Arrhenius plot = -9.13×10^3 $^\circ$A, and at $1/T = 2.0 \times 10^{-3}$ $(^\circ A)^{-1}$, $\log_{10}$ k = -2.985. Hence equation of line is:-

$$\log_{10} k = 15.275 - 9.13 \times 10^3 \left(\tfrac{1}{T}\right) \qquad \dots\dots (6)$$

giving an activation energy E = 41.5 K cals. mole^{-1}.

(ii) Dehydrochlorination in Air

The slope of Arrhenius plot = -7.86 x 10^3 °A, and at $1/T$ = 2.0 x 10^{-3} (°A)$^{-1}$, $\log_{10}$ k = -2.790. Hence equation of line is:-

$$\log_{10} k = 12.93 \; -7.86 \times 10^3 \left(\frac{1}{T}\right) \qquad \qquad \ldots\ldots (7)$$

giving an activation energy E = 36.1 K cals. mole^{-1}.

Table 3. Values of $\log_{10}$ k and $1/T$ for
Dehydrochlorination in Nitrogen

Sample Temperature (°C)	$1/T$ (°A)$^{-1}$ x 10^{-3}	$\log_{10}$ k
267	1.851	-1.678
256	1.890	-1.971
243	1.937	-2.392
232	1.980	-2.815
224	2.012	-3.036
219	2.032	-3.357

Table 4. Values of $\log_{10}$ k and $1/T$ for
Dehydrochlorination in Air

Sample Temperature (°C)	$1/T$ (°A)$^{-1}$ x 10^{-3}	$\log_{10}$ k
272	1.834	-1.490
257	1.886	-1.899
243	1.937	-2.277
232	1.980	-2.572
224	2.012	-3.011
212	2.061	-3.332

4. CALCULATED DEHYDROCHLORINATIONS

a) Isothermal Dehydrochlorination

The time taken for PVC to release a percentage (P) of the theoretical hydrogen chloride is given by equation (3) namely that

$(100-P)^{-\frac{1}{2}}$ = 0.1 + $\frac{1}{2}$kt where t is the decomposition time in minutes. The rate constant k for the dehydrochlorination in air or nitrogen for a particular temperature may be derived from the Arrhenius equations (equations 6 and 7) or the Arrhenius plot in Figure 9. However, for convenience, the

rate constants have been plotted logarithmically as direct functions of the temperature in degrees centigrade in Figure 10.

As an example and to assist other current studies of the dehydrochlorination of PVC[1,5], Table 5 shows the calculated times for 25, 50 and 75 per cent of theoretical dehydrochlorination in air and nitrogen between 200 and 300°C. The relevant equations are given in Appendix 1.

Table 5. Times for 25, 50 and 75 per cent of theoretical dehydrochlorination.
Dehydrochlorination Time (min)

Temperature (°C)	25 per cent		50 per cent		75 per cent	
	Nitrogen	Air	Nitrogen	Air	Nitrogen	Air
200	322	148	855	396	2065	956
220	53.1	31.0	142	82.8	342	200
240	9.9	7.43	26.4	19.6	63.9	47.9
260	2.18	2.04	5.65	5.46	13.65	13.2
280	0.52	0.58	1.38	1.54	3.35	3.72
300	0.14	0.19	0.36	0.49	0.66	1.21

b) Dehydrochlorination during non-linear temperature profiles

(i) General Theory

In this report, the dehydrochlorination of PVC has been studied in detail under isothermal conditions. In fires, PVC materials are subjected to conditions where the temperature increases in a non-uniform manner. The temperature profile depends upon many experimental fire parameters such as the ventilation, the fuel load and the position of the PVC relative to the fire.

The rate of release of hydrogen chloride during these changes may be calculated with some degree of approximation by representing the temperature profile as a series of short time intervals with a constant mean temperature throughout each interval. In this way the extent of dehydrochlorination at any experimental time is built up by a summation of the dehydrochlorination in all preceding isothermal time intervals.

Assume that $(100-P_0)$ and $(100-P_1)$ represent the percentages of the available hydrogen chloride in a sample of PVC at the beginning and end respectively of a time interval t_0 to t_1. Then from equation (3):-

$$(100-P_0)^{-\frac{1}{2}} - (100-P_1)^{-\frac{1}{2}} = \frac{k_{0.1}}{2} \ (t_0 - t_1)$$

where $k_{0,1}$ is the rate constant for the mean temperature of the interval.

Assume further that this time interval is chosen at a relatively low temperature, such that $P_0 \doteq 0$. Thus for the period t_0 to t_1:-

$$(100-P_1)^{-\frac{1}{2}} = 0.1 - \frac{k_{o,1}}{2}(t_0 - t_1)$$

or

$$(100-P_1)^{-\frac{1}{2}} = 0.1 + \frac{k_{o,1}}{2} \Delta t_{o,1}$$

Where
$$\Delta t_{o,1} = -(t_0 - t_1)$$

Also for the next successive time interval t_1 to t_2:-

$$(100-P_2)^{-\frac{1}{2}} = (100-P_1)^{-\frac{1}{2}} + \frac{k_{1,2}}{2} \Delta t_{1,2}$$

or

$$(100-P_2)^{-\frac{1}{2}} = 0.1 + \frac{k_{o,1}}{2} \Delta t_{o,1} + \frac{k_{1,2}}{2} \Delta t_{1,2}$$

where $k_{1,2}$ and $\Delta t_{1,2}$ are defined in a similar manner as in interval t_0 to t_1. In general terms, and for convenience abbreviating $k_{i-1,i}$ and $\Delta t_{i-1,i}$ to k_i and Δt_i respectively we have

$$(100-P_n)^{-\frac{1}{2}} = 0.1 + \frac{1}{2} \sum_{i=1}^{i=n} k_i \Delta t_i \qquad \ldots\ldots (8)$$

where P_n is the total hydrogen chloride released at the end of interval i.

For a constant Δt, equation (8) becomes:-

$$(100-P_n) = 1/(0.1 + \frac{\Delta t_i}{2} \sum_{i=1}^{i=n} k_i)^2 \qquad \ldots\ldots (9)$$

Hence the variation of P_n with time may be calculated.

(ii) Comparison of Calculated and Experimental Dehydrochlorination

Temperature programming facilities were not readily available on the decomposition furnace for experimental studies of the dehydrochlorination under various temperature-time profiles. However, as a test, one experiment was performed where the furnace was allowed to warm up under low power to a temperature in excess of $300^\circ C$ and the release of hydrogen chloride from a sample of PVC monitored over the critical period between 200 and $300^\circ C$. For this experiment the rate of heating was carefully adjusted to give the rise from 200 to $300^\circ C$ in about 15 minutes. The temperature-time profile of the sample decomposed in nitrogen is shown in Figure 11. The temperature profile was

recorded as furnace control temperature with time and related to sample temperature from the data of Figure 4. The observed release of hydrogen chloride, as percentage of the theoretical, with time is plotted in Figure 12. Zero time corresponds to the injection of the boat into the furnace and is essentially an arbitrary origin.

The data for the calculated extent of dehydrochlorination are shown in Appendix 2 and shown graphically in Figure 12. For this calculation the temperature-time profile (Figure 11) is divided into 1-minute intervals (i.e. $\Delta t = 1$) as in column I. For each time interval an arithmetic mean temperature is recorded from Figure 11 and shown in column II. For each mean temperature a mean rate constant k_i is obtained from Figure 10 and tabulated in column III. From this data the value of $0.1 + \dfrac{\Delta t_i}{2} \sum_{i=1}^{i=n} k_i$ and hence P_n may be calculated as a function of time. It should be noted that the values given for P_n refer to the extent of dehydrochlorination at the end of each time interval. Column I records the time of the start of each interval. Time intervals with mean temperatures below 200°C are not included in the calculation since dehydrochlorination at these temperatures is very slow.

In Figure 12, the general shape of the calculated and experimental curves are very similar but there is a difference of about 2 minutes between the two. The experimental curve should lag behind the calculated curve because of the collection time lag of approximately 0.75 min (i.e. the time taken for the hydrogen chloride released from the PVC to be carried to the collection system by the nitrogen flow). A time lag of more than 0.75 minutes probably indicates that the temperature of the sample lags behind the recorded value during the programming.

5. DISCUSSION

The dehydrochlorination of PVC has been studied in air and nitrogen over the temperature range 200 to 300°C. In nitrogen the release of hydrogen chloride can be represented by a 3/2 order decomposition up to about 80 per cent of theoretical dehydrochlorination. As reported on page 5, some linearity was found for both a first and a second order plot but the 3/2 order extended the linearity to the widest range of dehydrochlorination.

It is known that the dehydrochlorination is a complex elimination process[1,3] and in many ways it is surprising that the decomposition can be represented by simple kinetic laws. It is now generally accepted that the elimination of

hydrogen chloride involves a 'zip' dehydrochlorination with chlorine atoms as the chain carriers. There are some doubts about the chain initiation step and it is probable that the chain sequence is initiated by a radical produced at a structural defect rather than from a direct C-Cl split. Chain terminations occur at abnormalities in the chain such as cross linking points, or by radical loss.

In air, the relationship for a 3/2 order decomposition is comparatively poor. Oxygen is known to play an important role in the decomposition and probably produces an increase in the number of initiation sites. The work outlined in this report has been concerned with the dehydrochlorination of a commercial PVC as small cubes (approximately 3 mg each) where the diffusion of oxygen to the majority of the mass may be restricted. This diffusion will depend on the degree of decomposition (i.e. extent of the charring) and the rate of release of hydrogen chloride which could alter the kinetics of decomposition throughout an experiment.

The activation energies for decompositions in nitrogen and air have been calculated from the Arrhenius plots as 41.5 and 36.1 K cals. mole^{-1} respectively. These are somewhat larger than the reported values of around 25 to 35 K cals. mole^{-1}. (See section 1 (b)) for the decomposition of the PVC polymer. The larger values reported in this work probably arise from the use of stabilisers in the commercial material.

However, these values are much lower than the C-Cl bond strength[6] of 74 K cals. mole^{-1}, confirming that initiation does not start with a C-Cl bond split. If, as suggested in the literature, the radical for the zip dehydro-chlorination is produced at a structural defect such as an oxygenated species in the polymer chain, then there may be several types of initiation process each having a different activation energy. The recorded values in this report may be mean activation energies.

There is some evidence, particularly in the kinetic plots of Figures 6 and 8, that the final level of dehydrochlorination is temperature dependent. This again may be attributed to various initiation mechanisms with a spread of activation energies. At the low temperature decomposition, the dehydrochlorination may involve only initiation processes having the smallest activation energy. As the temperature is increased, further initiation sites may become important.

Unfortunately time did not permit a full investigation of this problem. It was hoped to study the dehydrochlorination at relatively low temperatures (i.e. 200 to 250°C) over a long period of time to see if the hydrogen chloride

yield approached a final level much less 100 per cent of the theoretical. However in practical situations, as in fires the temperature rises rapidly and the overall time of interest rarely exceeds the 50 minutes studied in this report. Consequently the dehydrochlorination over long periods of time was not undertaken.

In general, the work of this report provides the relevant data for calculating the release of hydrogen chloride from a knowledge of the temperature-time profile of the PVC. This calculation is relatively straightforward for isothermal decompositions and a method for predicting the release of hydrogen chloride during non-linear temperature increases, as in fires, has been derived.

It has been shown that the rate of release of hydrogen chloride is to some extent dependent upon the oxygen concentration near the PVC. In fires the concentration of oxygen is controlled by many experimental parameters, particularly the ventilation and fuel loading and can vary from a nominal 20 per cent to as low as a few per cent. In a well ventilated fire, where there is an ample supply of oxygen, the release of hydrogen chloride may be calculated using the data recorded in this report in air. In fires of low ventilation the oxygen concentration can fall rapidly and it is not easy to incorporate atmospheric changes of this kind into the kinetic analysis. A reliable solution to the problem is to calculate two dehydrochlorination curves assuming firstly an air atmosphere and then secondly a nitrogen atmosphere. The actual dehydrochlorination curve will lie between these two limits. In practice these limits are not widely separated.

Finally, it should be emphasized that the dehydrochlorination of PVC is essentially a thermal decomposition. Flaming and combustion are not required and the amount of hydrogen chloride released from a sample depends upon the temperature-time history of the sample. This work should therefore be of value in estimating the hydrogen chloride production in problems such as the over-heating of electrical equipment as in computers, telephone equipment and cable ducting. This information is relevant for studies of toxicity and corrosion.

6. CONCLUSIONS

1. In nitrogen, the thermal decomposition of a commercial PVC has been represented over a wide range of dehydrochlorination as a 3/2 order decomposition.

2. In air, this 3/2 order is less accurate than in nitrogen but acceptable for practical applications contemplated here.

3. The activation energies for the decomposition in nitrogen and air are 41.5 and 36.1 K cals. mole^{-1} respectively.

4. The data can be used to predict the dehydrochlorination of PVC in fires and allied problems purely from a knowledge of the temperature-time history of the material.

7. REFERENCES

1. WOOLLEY, W. D. A Study and Toxic Evaluation of the Products from the Thermal Decomposition of PVC in Air and Nitrogen, F.R. Note No.769, July 1969.

2. See MADORSKY, S. L. Thermal Degradation of Organic Polymers, Interscience Publishers, 1964, p.160-167.

3. GEDDES, W. C. Mechanism of PVC Degradation, Rubber Chemistry and Technology, 1967, 40 (1), p.177-215.

4. See BENGOUGH, W. I. Weathering and Degradation of Plastics, Editor Pinner S.M., Columbine Press 1966, p.70.

5. STARK, G. W. V., EVANS, W., and FIELD, P. Toxic Gases from Rigid PVC in Fires, F.R. Note No.752, March 1969.

6. COTTRELL, T. L. The Strength of Chemical Bonds, Butterworths Scientific Publications, 1954, p.209.

APPENDIX 1

Time for 25, 50 and 75 per cent dehydrochlorination given by:-

$$t_{25} = 0.0310/k$$

$$t_{50} = 0.0828/k$$

$$t_{75} = 0.20/k$$

APPENDIX 2

Calculated Dehydrochlorination

I Start of time interval (min)	II Mean temperature ($^{\circ}$C)	III Mean rate constant (k_i) (Per cent$^{-\frac{1}{2}}$ min^{-1})	IV $0.1 + \dfrac{\Delta t_i}{2} \sum\limits_{i=1}^{i=n} k_i$ (Per cent$^{-\frac{1}{2}}$)	V $100-P_n$ (Per cent)	VI P_n (Per cent)
4	203	0.00012	0.10006	100	0
5	211	0.00026	0.10019	100	0
6	219	0.00055	0.10046	99.1	0.9
7	227	0.00110	0.10101	98.1	1.9
8	232	0.00165	0.10183	96.9	3.1
9	238	0.00270	0.10318	94.0	6.0
10	242	0.0037	0.10488	91.1	8.9
11	248	0.0058	0.10778	85.1	14.9
12	253	0.0080	0.11178	80.1	19.9
13	258	0.0129	0.1182	71.8	28.2
14	263	0.018	0.1272	61.9	38.1
15	268	0.026	0.1402	50.9	49.1
16	272	0.035	0.1572	40.5	59.5
17	276	0.046	0.1802	30.8	69.2
18	279	0.056	0.2082	23.1	76.9
19	283	0.074	0.2452	16.7	83.3
20	288	0.102	0.2962	11.4	88.6
21	291	0.125	0.3582	7.80	92.20
22	295	0.160	0.4382	5.21	94.79
23	298	0.195	0.5352	3.50	96.50
24	302	0.250	0.6602	2.29	97.91
25	305	0.300	0.8102	1.52	98.48
26	307	0.340	0.9802	1.04	98.96
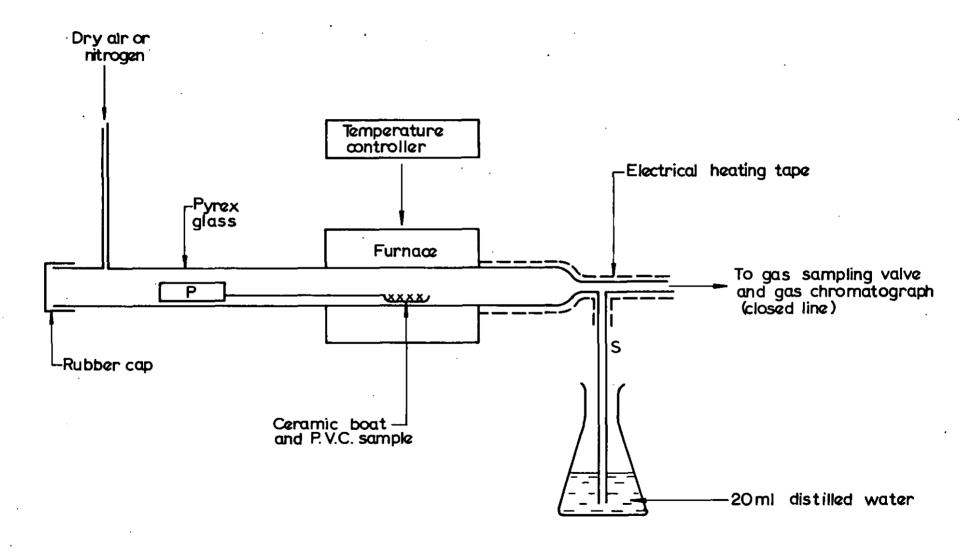
FIG. 1. THE DECOMPOSITION SYSTEM
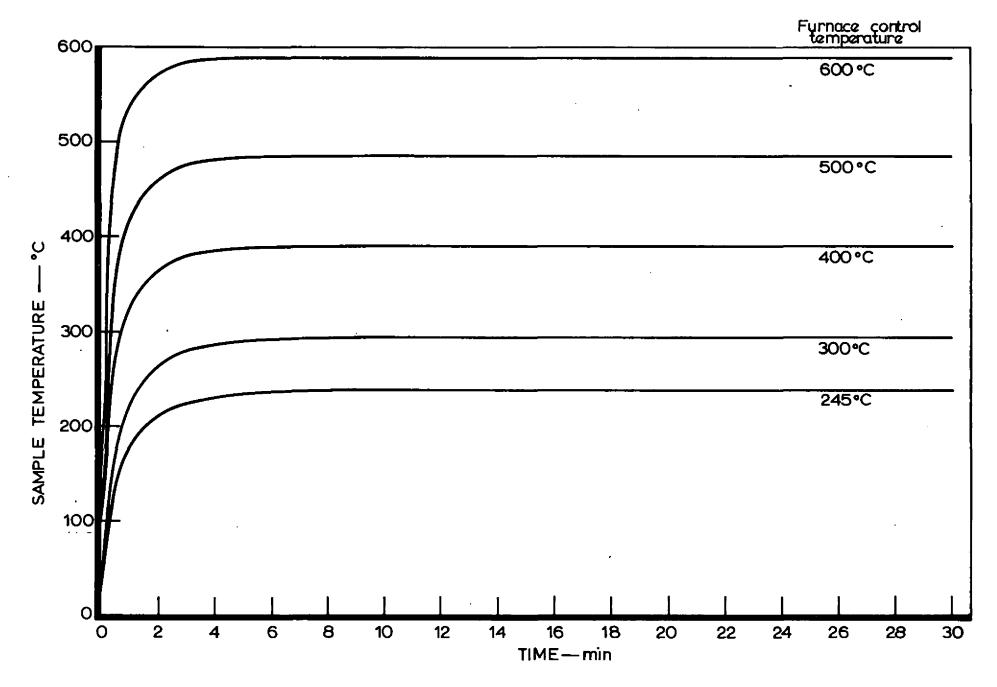
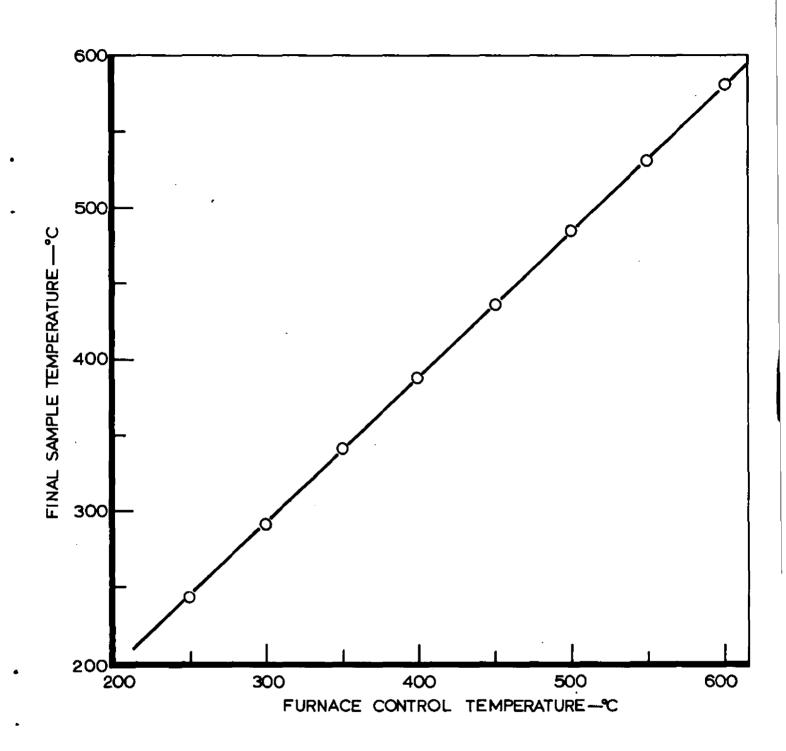FIG. 2. TEMPERATURE PROFILES OF SAMPLES INJECTED INTO THE FURNACE

FIG. 3. RELATIONSHIP BETWEEN FINAL SAMPLE TEMPERATURE
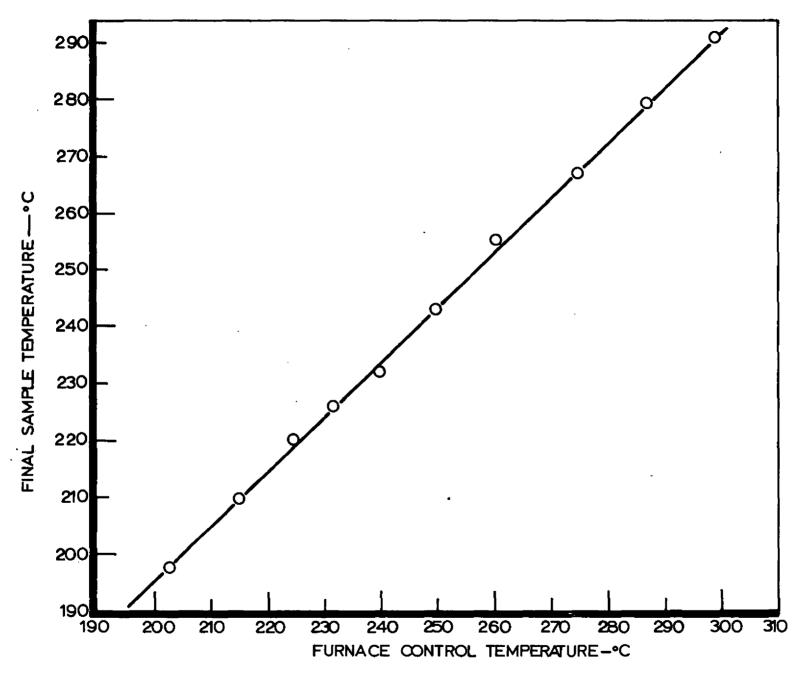AND FURNACE CONTROL TEMPERATURE

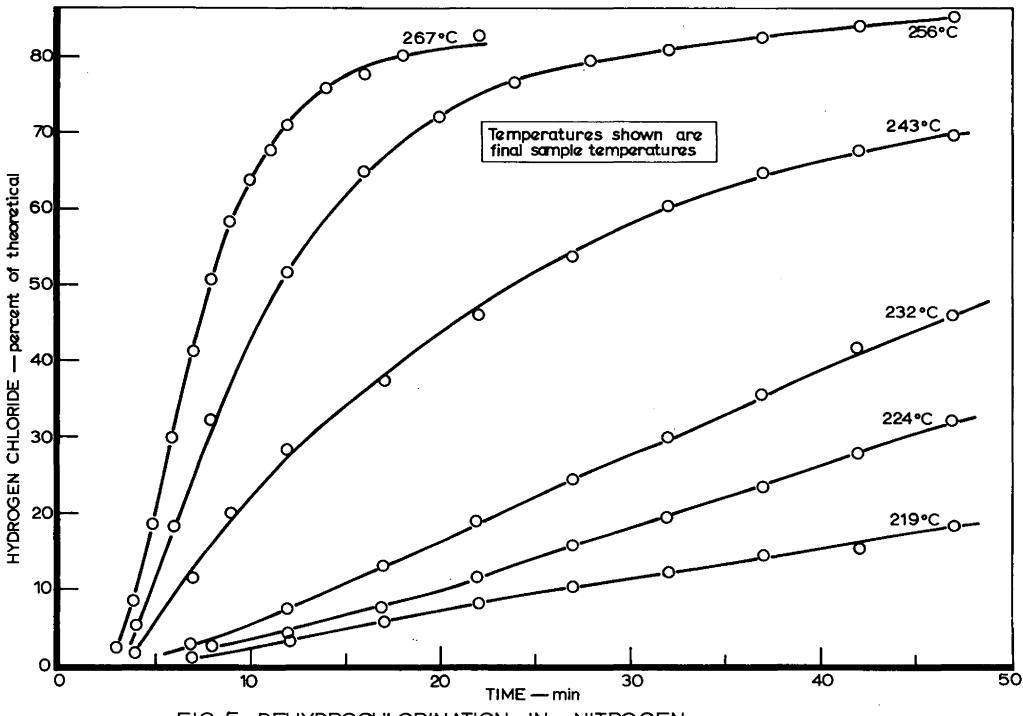FIG. 4. RELATIONSHIP BETWEEN FINAL SAMPLE TEMPERATURE AND FURNACE CONTROL TEMPERATURE

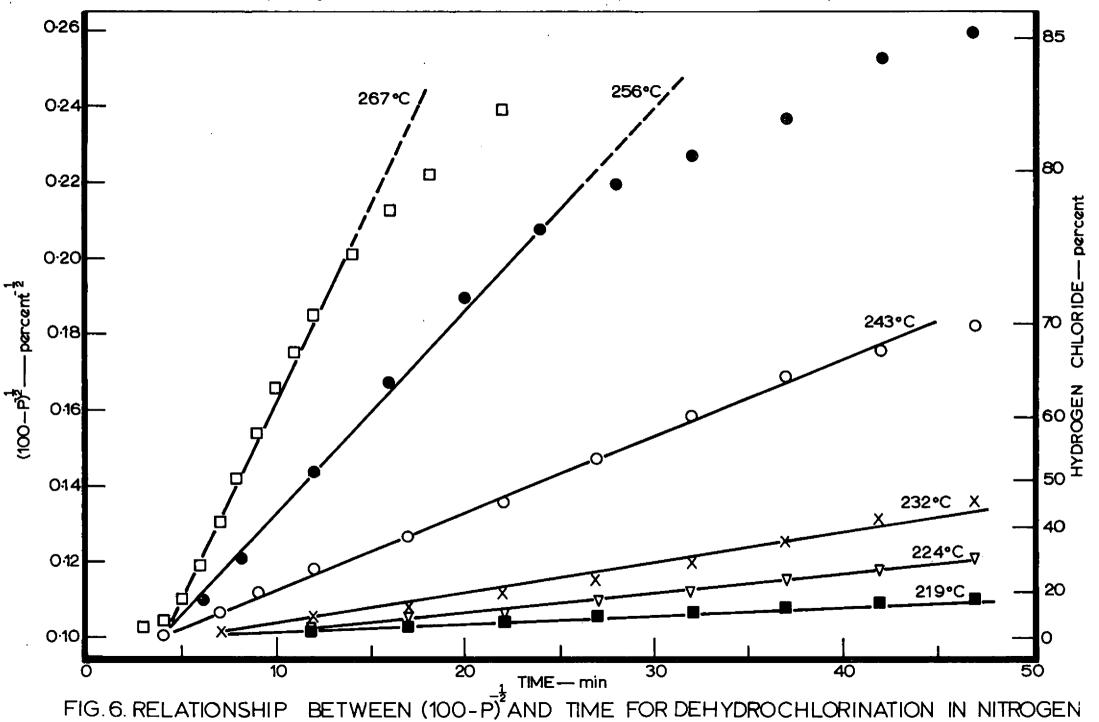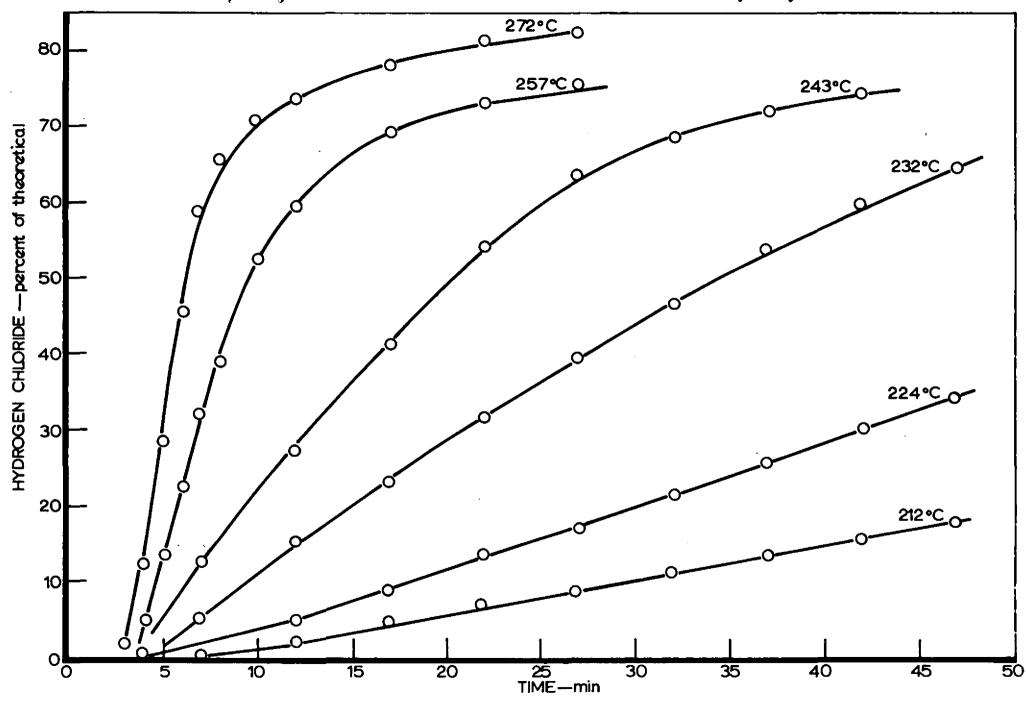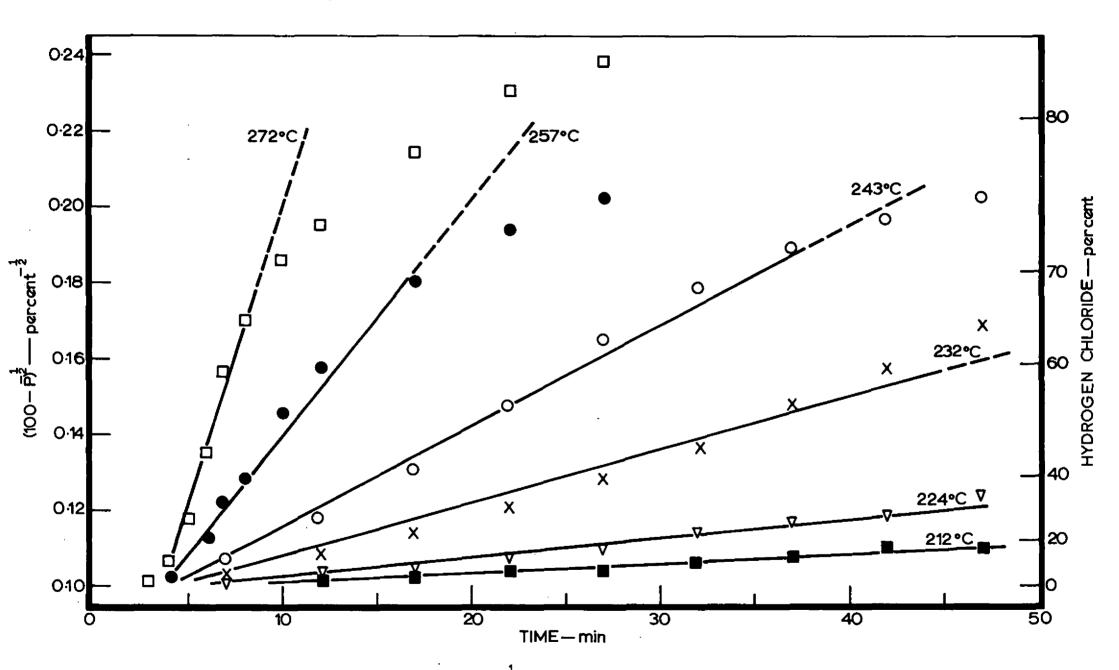FIG. 5. DEHYDROCHLORINATION IN NITROGEN

FIG. 6. RELATIONSHIP BETWEEN $(100-P)^{-\frac{1}{2}}$ AND TIME FOR DEHYDROCHLORINATION IN NITROGEN

FIG. 7 DEHYDROCHLORINATION IN AIR

FIG.8. RELATIONSHIP BETWEEN $(100-P)^{-\frac{1}{2}}$ AND TIME FOR DEHYDROCHLORINATION IN AIR
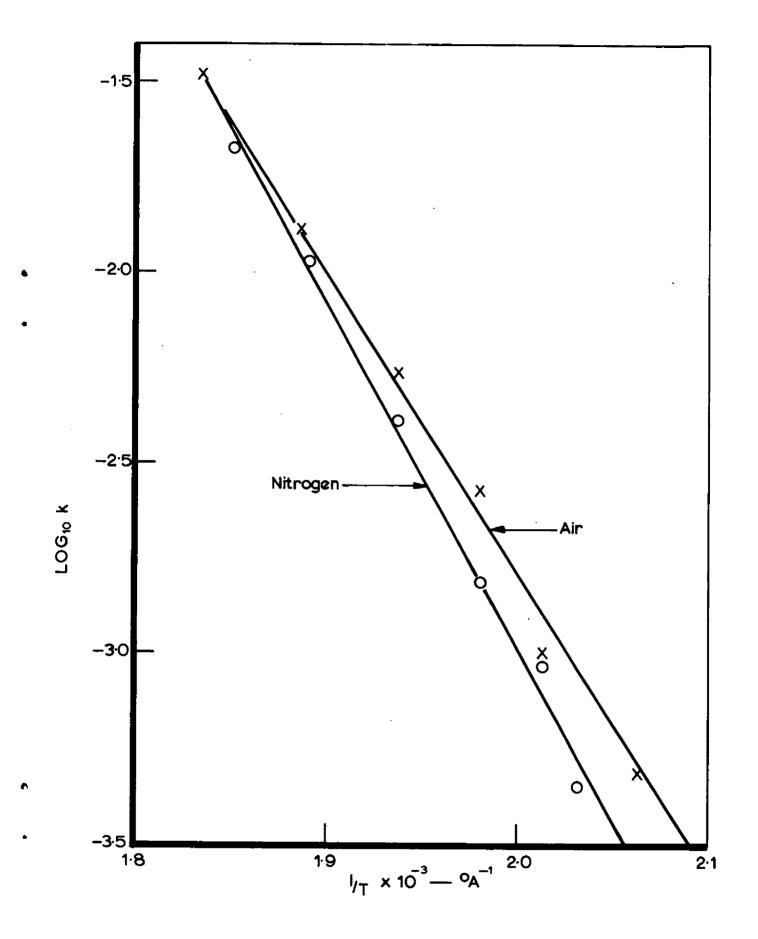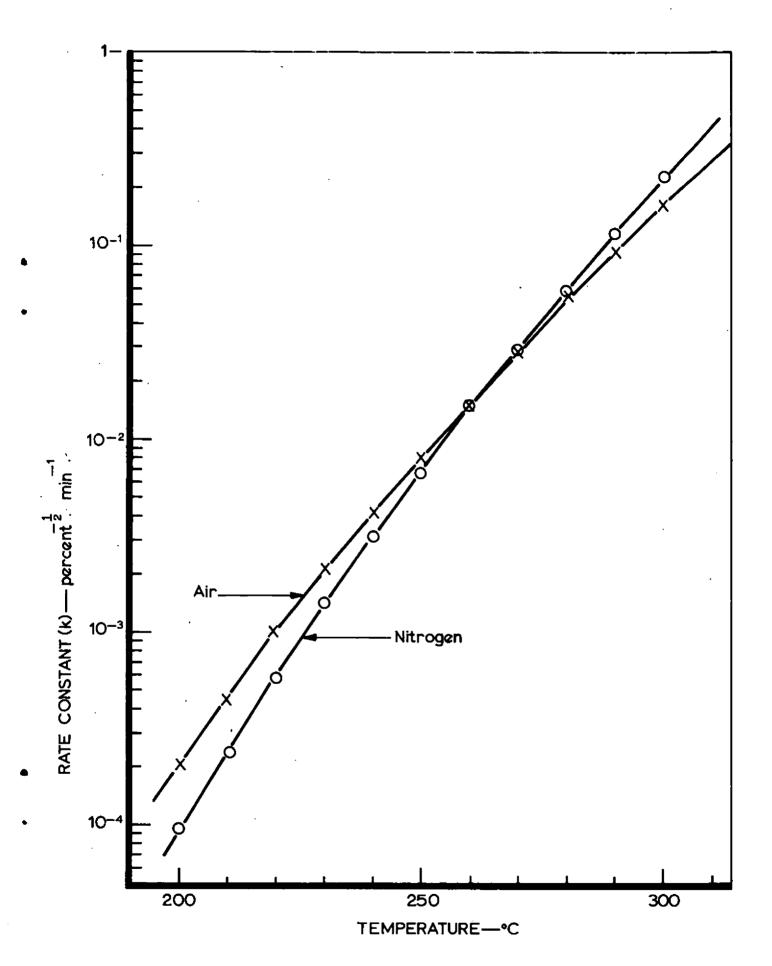
FIG. 9. ARRHENIUS PLOTS FOR DEHYDROCHLORINATION
IN NITROGEN AND AIR

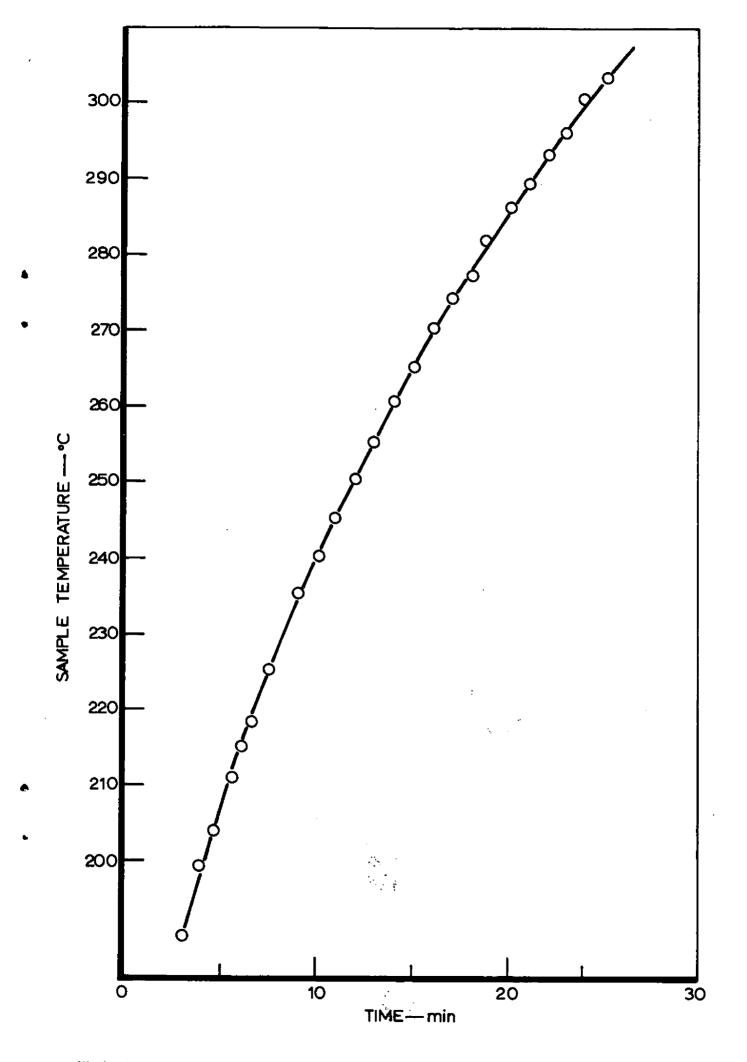FIG.10. RATE CONSTANTS AS A FUNCTION OF TEMPERATURE
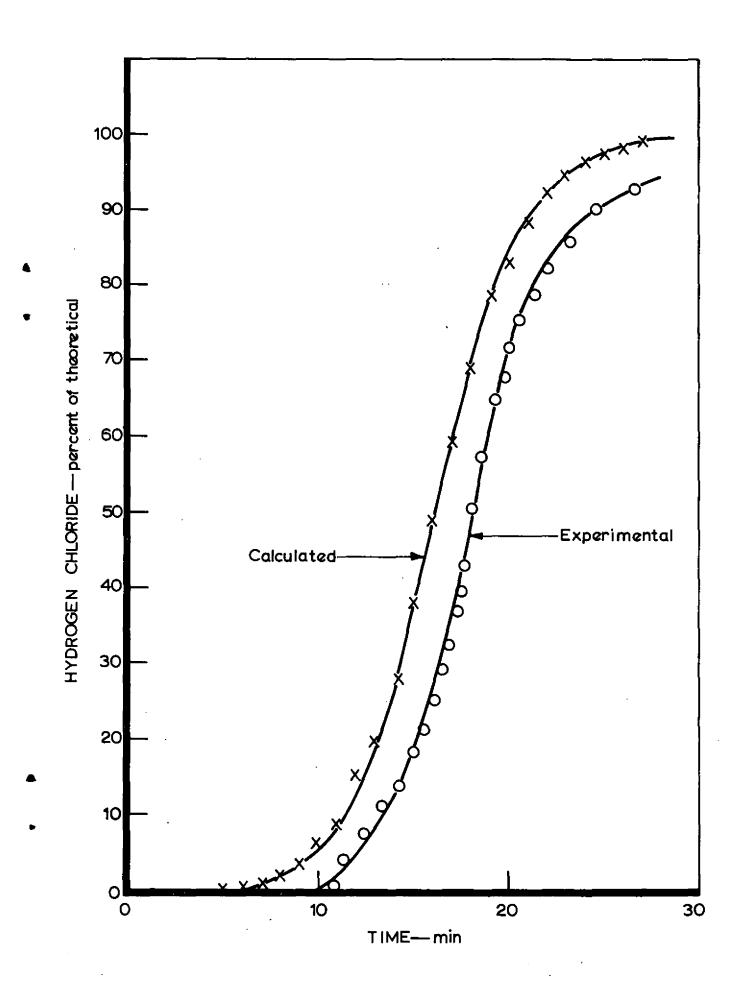
FIG. 11. TEMPERATURE PROGRAMME OF SAMPLE IN FURNACE

FIG. 12. CALCULATED AND EXPERIMENTAL DEHYDROCHLORINATION