

A THESIS

entitled

THE INFLUENCE OF ADDITIVES ON THE
THERMAL DEGRADATION AND OXIDATION
OF POLYETHYLENE

submitted by

DAVID JOHN SMITH

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ABSTRACT

This thesis describes an investigation into the thermal and oxidative degradation of polyethylene and into the influence on these reactions of the presence of bromine-containing additives in the atmosphere surrounding the polymer. The thermal degradation reaction was studied at both 400 and 430°C and the oxidation reaction was studied at 430°C

In the Introduction a survey is made of previous studies of the thermal and oxidative degradation of polyethylene and other organic polymers. Work on the influence of bromine-containing additives on the flammability of organic polymers is also discussed together with relevant work on the combustion of volatile hydrocarbons.

The techniques and apparatus used are described in the Experimental Section. A static system was used which incorporated a reaction vessel designed specifically for the introduction of solid polyethylene samples into the system. The reactions were followed by pressure change and loss of weight measurements and by analysis of the volatile products of the reactions.

The Results Section gives details of the kinetic and analytical results obtained. Hydrogen bromide reduces the rate of loss of weight of polyethylene during thermal degradation at both 400 and 430°C whereas this additive increases the rate of breakdown in the gas phase of the volatile products formed from the polymer. The rate of degradation of polyethylene was also found to be reduced by those organic bromides which decomposed to yield hydrogen bromide under

the experimental conditions used. Hydrogen bromide reduced the rate of loss of weight of polyethylene during oxidation whereas the rate of oxidation of the volatile products formed from the oxidising polymer was increased by this additive.

The experimental results are critically examined in the Discussion. The reduced loss of weight of the polymer during both thermal and oxidative degradation in the presence of hydrogen bromide is discussed in the light of the possible physical and chemical effects of this additive. On the basis of a proposed chain mechanism for the thermal degradation of polyethylene, the influence of hydrogen bromide is attributed to an increased rate of chain termination in the presence of this additive. It is suggested that a similar effect may also contribute to the observed reduction of the rate of loss of weight during oxidation of the polymer. Finally the relevance of this work to the influence of additives on the flammability of polyethylene is discussed.

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A General

The degradation of organic polymers may be brought about by a variety of chemical and physical agencies and this process is often accompanied by an unfavourable change in the physical and mechanical properties of the polymer. Degradation in this context is taken specifically to mean a reduction in the lengths of the polymer chains although other changes in structure, such as cross-linking or loss of groups attached to the chain, may also have a profound effect on the bulk properties of the material. Physical agencies which are known to cause chain scission include infra-red, ultra-violet and gamma radiation, heat, light, ultrasonic waves and mechanical stress. Many previous investigations of degradation induced by chemical agencies have been specifically concerned with attack by oxygen.

The study of degradation processes has proved to be of fundamental importance in polymer chemistry often showing, for example, how small irregularities in molecular structure may have a pronounced effect on the behaviour of the polymer. Basic research has, however, been stimulated by two requirements associated with the use of polymeric materials. The first is that the material should be stable in the environment in which it is to be used and the second is that the flammability of the material should be reduced as far as possible so that it does not present an unreasonable fire hazard. The environmental problem arises even in the fabrication of commercial materials (in processes such as moulding, rolling, extrusion etc.), where both thermal degradation, or the incorporation of oxygenated

structures which cause subsequent degradation during use, may occur. At the other extreme, polymeric materials are often required for use at very high temperatures so that the synthesis of materials which are thermally stable but still retain desirable mechanical properties is becoming increasingly important (1).

The flammability of a polymer depends on both its thermal stability and its resistance (or that of its degradation products) to oxidation. Since the problem which formed the background to the original work which is described in this thesis concerned the flammability of polyethylene, the introductory section reviews published work on the thermal and oxidative degradation of organic polymers. Work on polymers other than polyethylene is described either where comparison with work on polyethylene is useful or where information of a comparable nature on polyethylene is not available.

B Thermal degradation of organic polymers

1. The nature of the problem and general experimental methods

For the elucidation of the mechanism by which organic polymers are degraded by heat, measurements of the following are of vital importance.

- (i) The change of the molecular weight of the polymer during degradation.
- (ii) The nature of the products of degradation.
- (iii) The rates and temperature coefficients of the degradation processes.

At temperatures where the rate of degradation is appreciable, however, many polymers exist in the liquid (often viscous) state, so that the samples are subject to effects which may make meaningful quantitative measurements difficult. Thus, since polymers tend to be poor conductors of heat, a sample may, where a degradation process is endothermic, be below the temperature of that of the surrounding reaction area (2). In measuring product formation, especially with thick polymer samples at low temperatures, volatile products may take many seconds to escape from the polymer during which time secondary reactions may occur (3). On the other hand, at high temperatures the polymer may be partly, if not entirely, degraded before the supposed reaction temperature is reached and the products will be even more liable to secondary cracking (4). With these effects in mind, investigators have tended to keep the polymer samples small and to allow the samples to undergo pyrolysis under vacuum so that the products are removed as quickly as possible from the reaction zone. Very little work has been reported on the pyrolysis of polymers in gaseous atmospheres and that which has been done has dealt mainly with product formation.

The general techniques by which the course of the degradation of polymers has been followed include those summarised below.

(i) Loss of weight This is applicable at temperatures where volatile fragments are produced during pyrolysis and may be followed either by withdrawing the polymer sample during pyrolysis (5) or by incorporating a sensitive balance in the apparatus so that loss of weight may be measured continuously (6,7). In most work of this

nature the sample is maintained at a constant temperature throughout each run but more recently a non-isothermal method has been successfully devised (8).

(ii) Product formation Measurement of pressure increase during pyrolysis is useful only where the polymer is degraded almost entirely to give very low molecular-weight products (2). On the other hand, qualitative and quantitative analysis, by mass spectrometry or gas chromatography, of the volatile products formed has proved important in the interpretation of the mechanism of degradation reactions.

(iii) Viscosity measurements The intrinsic viscosity of a polymer, obtained by measurements of the viscosities of solutions of the polymer in a suitable solvent, is related to its number average molecular weight. Thus, it is possible to determine by viscometry measurements the variation of the molecular weight of a polymer during degradation. Polyethylene is one of the few polymers for which this has been done (9).

(iv) Group analysis The formation of specific groups in the polymer residue may be determined at different stages of the degradation process (9).

2. The thermal degradation of polyethylene

(a) The thermal stability of polyethylene

In the absence of oxygen, polyethylene is stable up to 290°C when chain scission is found to take place producing a decrease in molecular weight (9). At 360°C volatile products begin to appear, while at higher temperatures (above 450°C) complete disintegration to

volatile products occurs so that there is no evidence of cross-linking (10).

(b) Molecular weight measurements

Oakes and Richards (9) followed the change in molecular weight (number average, M) as a function of time of heating by measuring the intrinsic viscosity, v , of the sample residues in tetralin. The molecular weight was obtained from the relationship,

$$v = 1.08(M)^{0.7} \times 10^{-3}$$

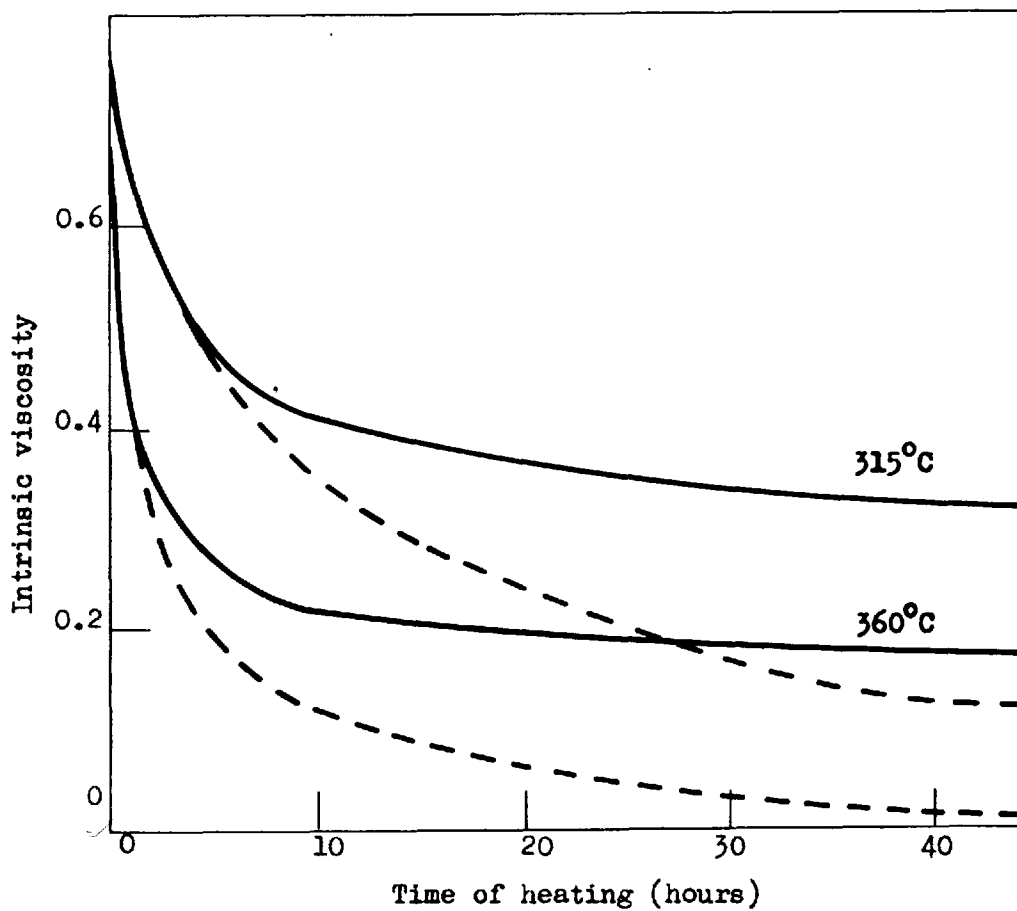
Samples of 5-10 g. were pyrolysed in glass tubes which were usually evacuated continuously but which were in a few cases filled with nitrogen. No difference could be detected between the rates of degradation of polymer samples pyrolysed in the evacuated and the nitrogen-filled tubes.

Measurements at 315 and 360°C, where no volatilisation occurs, indicated a sharp initial drop in molecular weight followed by a more gradual decrease tending towards a constant value. The variation of intrinsic viscosity with time which was obtained is shown in figure 1. Pyrolysis at higher temperatures produced a sharper fall in molecular weight.

From the variation of molecular weight, the number of C-C bonds broken could be calculated for given times of pyrolysis. The initial rate of degradation was expressed as the rate of breaking of C-C bonds. The dotted lines in figure 1 show the plots for the two temperatures which would be obtained if the initial rate of reaction were maintained throughout the reaction; comparison of the theoretical curves with the

Figure 1

Effect of time of heating on the intrinsic viscosity of a sample of polyethylene at 315 and 360°C (reference 9)



experimental curves shows that this is not the case. The activation energy obtained by Oakes and Richards (9) is compared with values obtained by other workers in section B.2(f).

Similar results were obtained by Wall and co-workers using polymethylene (11). In this work it was found that, at higher temperatures, where volatilisation of polymethylene occurred, the sharp initial drop in molecular weight was complete before one per cent of the polymer had volatilised.

(c) Group analysis of polyethylene residue

Oakes and Richards (9) examined the residue after pyrolysis and found it to be a polyethylene wax, similar to the original starting material, with an empirical formula corresponding closely to CH_2 . The degree of unsaturation of the product was determined by the measurement of its iodine number and the types of unsaturation were distinguished from the infra-red absorption spectrum. The results obtained confirmed and extended previous work by Thompson and Torkington (12).

It was found that the degree of unsaturation of the residue increased as pyrolysis proceeded. The molecular weights and iodine numbers of various product samples of differing molecular weight were determined and calculation showed that for the bulk of the reaction, degradation produced one double bond in each product molecule. It was concluded, therefore, that the primary products of degradation were monoalkenes. Infra-red absorption measurements indicated that three distinct types of alkenes were produced by pyrolysis, viz: (i) $\text{RCH}=\text{CH}_2$ (ii) $\text{RCH}=\text{CHR}$: (iii) $\text{RRC}=\text{CH}_2$. Of these, (ii) and (iii) increased to

a constant value by the time the molecular weight of the polyethylene had been reduced to 5-10 per cent of its original value and only the concentration of vinyl groups (type(i)) increased throughout the course of the reaction.

(d) The products of degradation

Madorsky and co-workers (10) studied the products formed during the pyrolysis of a commercial grade polyethylene (mol.wt.=20,000). 50 mg. samples of the polymer were pyrolysed in vacuo on platinum trays at various temperatures (335-450°C) and samples were taken for analysis after various pyrolysis times. The volatile products were condensed as the reaction proceeded on a surface cooled by liquid nitrogen and placed just above the pyrolysis tray. The products were later separated into three fractions, V_{pyr} , volatile at the temperature of pyrolysis, V_{25} , volatile at 25°C and V_{-80} , volatile at -80°C. The V_{-80} fraction, which formed about one per cent of the weight of polymer volatilised, was analysed by mass spectrometry and was found to consist of a complex mixture of C_1 - C_7 straight chain alkanes and alkenes with trace quantities of dienes. The monomer, ethylene, formed only 0.025 per cent by weight of the volatilised polymer. It was found that both the nature and relative quantities of the products in the V_{-80} fraction and the proportion of the total pyrolysed part accounted for by the V_{-80} fraction remained fairly constant over a wide range of volatilisation and reaction temperatures. The less volatile fraction, V_{25} , was presumed to consist of higher members of the alkane and alkene series. The fraction involatile at room temperature was found (by a freezing point method involving solution of the sample in camphor) to

have an average molecular weight of 700; this corresponds to a chain of approximately 50 carbon atoms.

Using the same technique the behaviour of polymethylene was investigated (13). No striking difference was noticed in the relative proportions of the three fractions or in the nature or quantities of the products in the V_{-80} fraction. Pyrolysis of polymethylene at higher temperatures (up to 1200°C) showed that the higher the temperature of pyrolysis the greater is the fragmentation of pyrolysis products. The introduction of an inert gas (e.g. helium, at atmospheric pressure) also increases the degree of fragmentation of the products (14,15). Madorsky (15) suggests that the effect of temperature may be ascribed to secondary reactions in which the primary products undergo degradation while passing through the hot zone of the reaction vessel. The effect of pressure may perhaps be accounted for in terms of molecular collisions hampering the escape of volatile products so that secondary reactions are again encouraged.

(e) Loss of weight measurements

The rate of production of volatile material from polyethylene has been investigated by Jellinek (6) and Madorsky (7) both of whom measured continuously the decrease in weight of the polymer undergoing degradation in a vacuum. Jellinek (6) used a quartz-spring balance and sample sizes of the order of 20 mg., whereas Madorsky (7) used a tungsten-spring balance and sample sizes of the order of 6 mg.

Jellinek (6) investigated three commercial polyethylenes of average molecular weight 11,000, 16,000 and 23,000. The results were

presented by plotting cumulative loss of weight as a function of time for temperatures varying between 370 and 436°C. Some of the results are given in figure 2. It can be seen that, for the major part of the reaction, linear plots are obtained; this indicates that the reaction is of zero-order with respect to the weight of polymer residue. The rate of the reaction was obtained directly from the loss of weight curve and expressed as per cent of original sample weight lost per minute. Some of the values obtained are given in table 1. It was found that, for a given pyrolysis temperature, the rate of loss of weight decreased with increase in the molecular weight of the starting material and this finding is in agreement with that of Oakes and Richards (9), who measured the initial rate of degradation in terms of bond scission.

Madorsky's results on polyethylene (mol. wt. = 20,000) are shown in figure 3. (The work is described in reference 7. The temperatures stated in the original reference were later corrected in reference 16. Figure 3 gives the corrected temperatures of pyrolysis). The rate of loss of weight, expressed as percentage change in the original sample weight per minute, is plotted against the weight per cent of polymer volatilised. Each pyrolysis curve appeared to consist of two distinct linear portions. The first portion of each curve corresponds to an initially high rate of loss of weight which rapidly decreases. The second portion of each curve corresponds to a more gradual decrease in the rate of loss of weight and the values which lie on the second part of each curve are found to correspond to a first-

Figure 2

Thermal degradation of 20 mg. samples of polyethylene (mol. wt. = 23,000). Cumulative loss of weight as a function of time (reference 6)

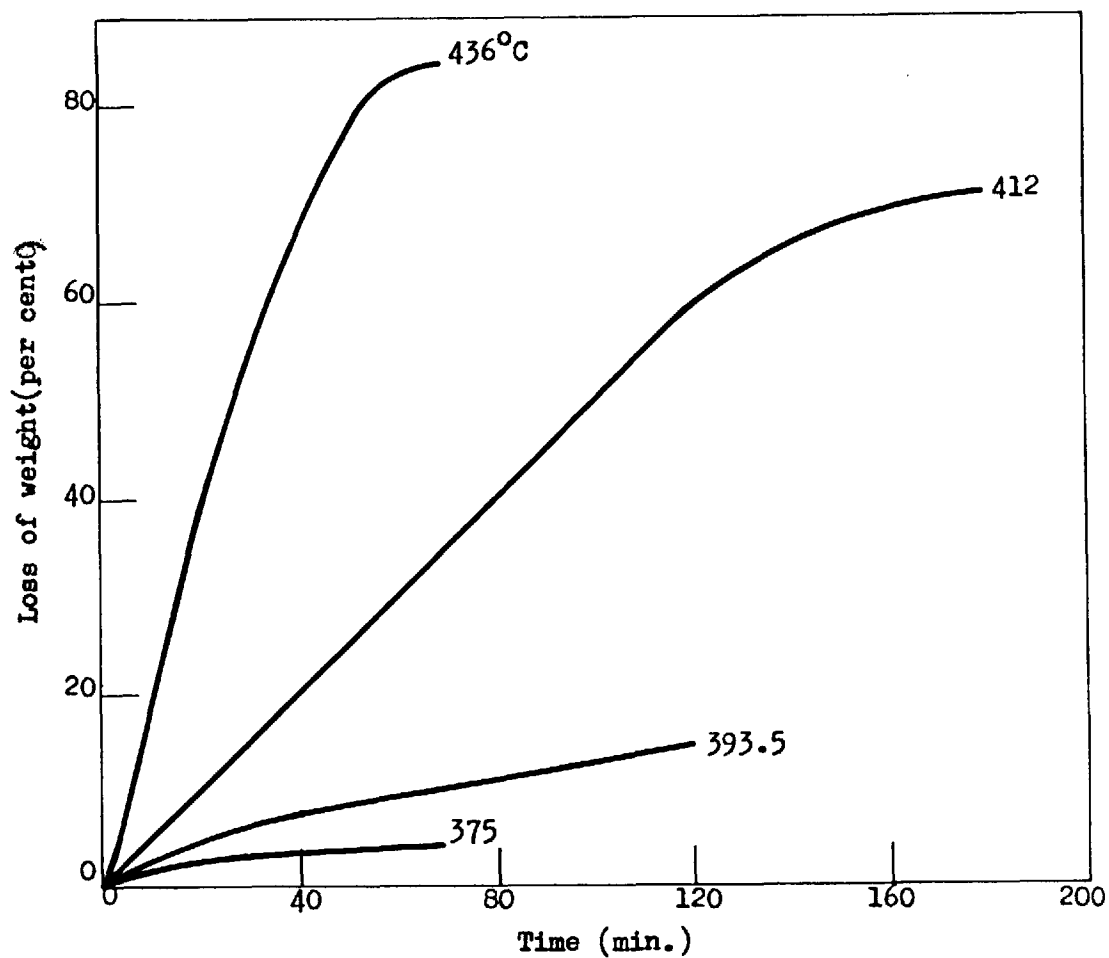


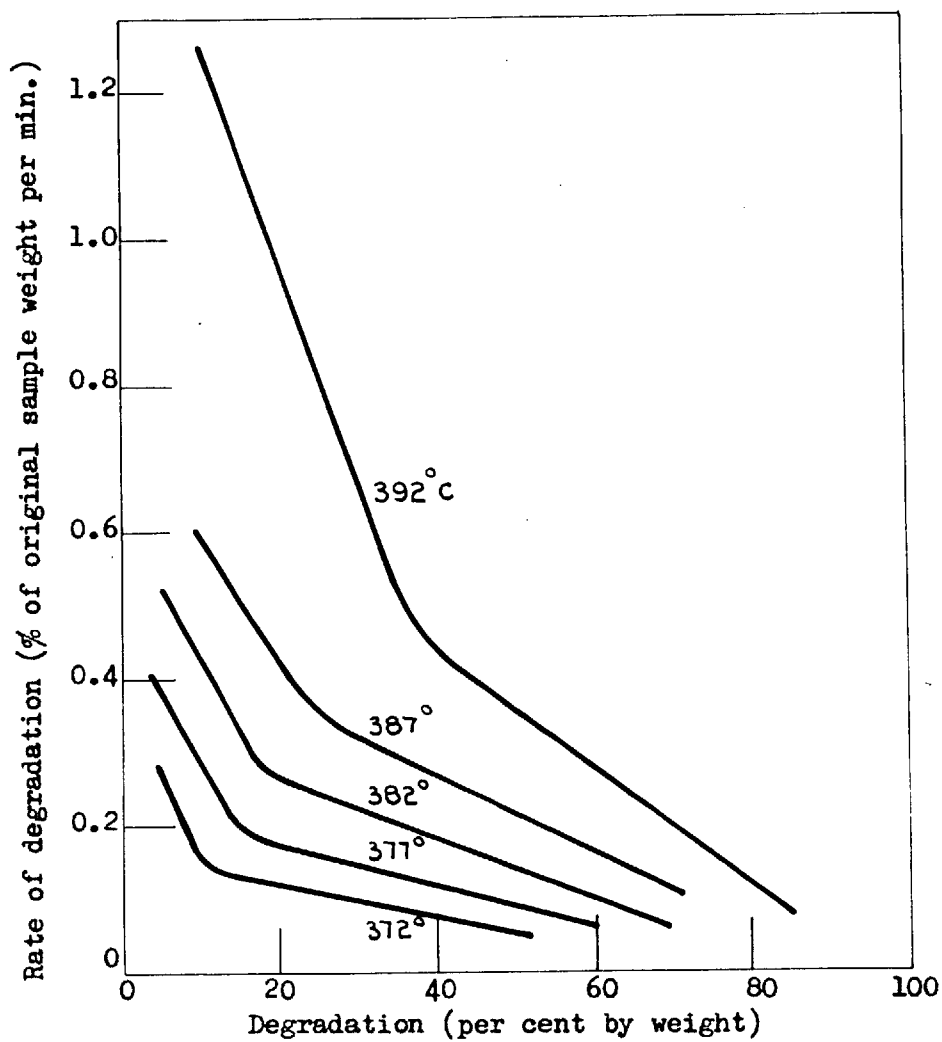
Table 1

Rate of thermal degradation of polyethylene measured by loss of weight

Molecular weight of sample	Temperature (°C)	Rate	
Madorsky (7)			
20,000		Initial rate (per cent of sample wt. min. ⁻¹)	Rate constant for first-order reaction (per cent of residue wt. min. ⁻¹)
	372	0.36	0.160
	377	0.45	0.225
	382	0.61	0.340
	387	0.78	0.480
	392	-	0.745
Jellinek (6)			
23,000		Rate of zero-order reaction (per cent of original sample wt. min. ⁻¹)	
	375	0.011	
	393	0.092	
	412	0.480	
	436	1.824	

Figure 3

Thermal degradation of 6 mg. samples of polyethylene.
Rate of loss of weight as a function of degradation
(reference 7)



order dependence on the weight of polymer residue. The discontinuity in the pyrolysis curve occurs at a higher percentage of volatilisation for higher pyrolysis temperatures. The initial rate of loss of weight of the polymer, expressed as the percentage of original sample weight lost per minute, was obtained from the intercept on the y-axis when the first portion of the curve was extrapolated. The first-order rate constant for the second portion of the curve was expressed as the percentage of residue weight lost per minute (i.e. $(-dw/dt)(1/w) \times 100$, where t is the pyrolysis time in minutes and w the weight of the residue at time t ; thus to obtain the more conventional rate constant the values should be divided by 100). The values obtained for the initial rates and for the first-order rate constants are given in table 1.

The results of Jellinek (6) and Madorsky (7) are not in very good agreement. They differ as regards the dependence of the rate on extent of pyrolysis and, although this makes difficult a comparison of the rates given in table 1, the values obtained by Madorsky (7) appear to be much higher than those obtained by Jellinek (6) at comparable temperatures. Jellinek did not observe a high initial rate although it may be relevant that before each experiment the polymer sample was heated in order to get it into a molten state. Criticism has been made of Jellinek's work in as much as by using relatively large sample weights, loss of weight may occur by sputtering, particularly in the later stages of pyrolysis, which would therefore obscure any decrease in the rate of loss of weight due to volatilisation (17). This might

account for the zero-order curves obtained.

Madorsky (7, 13,18) investigated the influence of the extent of chain-branching on the reaction by comparing the results obtained with the commercial polyethylene described above with those using a pure grade polymethylene (virtually no branched chains) (13) and a highly branched polyethylene (containing 20 methyl branches per 1000 carbon atoms) (18). The degradation of polymethylene was found to present an almost ideal case of first-order dependence of rate on the weight of polymer residue throughout the reaction. The results for the highly branched polymer resembled very closely those for the less branched commercial polyethylene, giving two distinct stages of reaction. For a given temperature the first-order rates of degradation obtained for the three polymers were about the same. Thus chain-branching appears to influence the reaction in the initial but not in the subsequent stages.

Anderson and Freeman (8) attempted to resolve the conflict evident in previous work using an elegant technique in which the loss of weight of polyethylene was measured continuously during pyrolysis under non-isothermal conditions. The temperature of a 100 mg. sample of polymer under vacuum was increased by 5°C per minute from ambient temperature to 500°C where pyrolysis was complete. From first derivatives of the weight loss - temperature curves it was possible to determine both the orders and the activation energies of different stages of the reaction. The technique allows the reaction to be studied immediately loss of weight occurs since it eliminates the time-lag in

the isothermal method during which the polymer reaches the proposed reaction temperature.

Anderson and Freeman (8) reported zero-order dependence of rate on residue weight from 0 to 15 per cent volatilisation. From 35 to 95 per cent volatilisation the reaction was first-order with respect to the residue. The region from 15 to 35 per cent volatilisation represented a transition from zero-order to first-order kinetics. Thus, Madorsky's observations on the later stages of the reaction appear to be confirmed although no evidence was produced in favour of a zero-order dependence of rate on residue for the initial stage. Since in Madorsky's work (7) the initial rate of the reaction was obtained by extrapolation, first-order kinetics were obviously assumed in this region.

In summarising the loss of weight work it appears probable that for most of the reaction the rate of loss of weight is proportional to the weight of residue. The dependence of the rate of pyrolysis on residue weight in the initial stage of the reaction still requires clarification.

(f) Activation energy

The activation energies for the thermal degradation of polyethylene obtained by various workers are given in table 2. In all but the work of Oakes and Richards (9), where the rate of carbon-carbon bond scission was determined, the rate of degradation was expressed in terms of loss of weight. In general the values are in very good agreement and it appears that, for the bulk of the pyrolysis reaction,

Table 2

The thermal degradation of polyethylene : values for the overall activation energy

Polymer	Extent of Reaction	Order with respect to residue	Activation energy (kcal mole ⁻¹)	Reference
Polyethylenes Mol.wt: 11,000-23,000	Initial rate only	-	60-70	9
Polyethylenes Mol.wt:	Bulk of reaction	zero		6
23,000			66.1	
16,000			52.6	
11,000			46.0	
Polyethylene Mol.wt: 20,000	Initial rate	first	48	7
	Later stages	first	63	
Polymethylene	Bulk of reaction	first	72	13
Branched polyethylene	Later stages	first	64	18
Polyethylene DYNH-1 Mol.wt:20,000	0-3% wt. loss	zero	48	8
	3-15%wt. loss	zero	61	
	35-95%wt.loss	first	68	

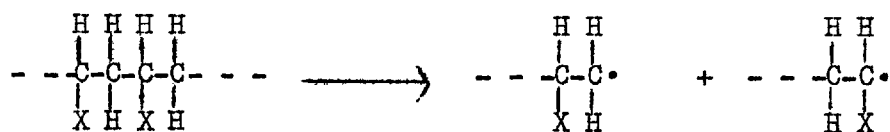
the overall activation energy for the degradation process is of the order of 60-70 kcal mole⁻¹.

(g) The reaction mechanism

Hydrocarbon polymer degradation reactions involve long chain molecules which may contain structural irregularities and any chemical change occurs in the condensed phase. Features such as these suggest that any established mechanism by which simpler hydrocarbon molecules undergo degradation may have little theoretical relevance to the detailed nature of polymer degradation. Since in each case the reactant is a hydrocarbon, however, the types of reaction and of intermediate species involved may well be similar.

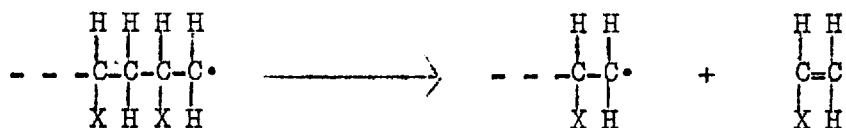
Before polymer degradation had received detailed attention, Rice and Rice (19) had suggested a mechanism for the gas phase degradation of simple hydrocarbons which involved the initial formation of free radicals and their subsequent participation in a chain reaction. Some years later, Simha et al. (20,21,22) proposed a similar mechanism for the thermal degradation of hydrocarbon polymers and this accounts fairly well for the general features of such reactions. The basic steps for the general case of an alkene polymer, (CHX)_n, are described below. (Note that in the equations the dotted line, - - - -, represents the continuation of the polymer chain.)

(i) Initiation



In a polymer such as a pure polymethylene initiation by chain scission could be caused only by thermal strain in the molecule. Most commercial polymers contain, however, small percentages of impurities and structural irregularities. In polyethylene, for example, oxygenated groups and chain branches have been detected by infra-red absorption measurements (12). Thus initiation may occur, at least in the early stages of the reaction, at points in the chain where such irregularities occur.

(ii) Propagation

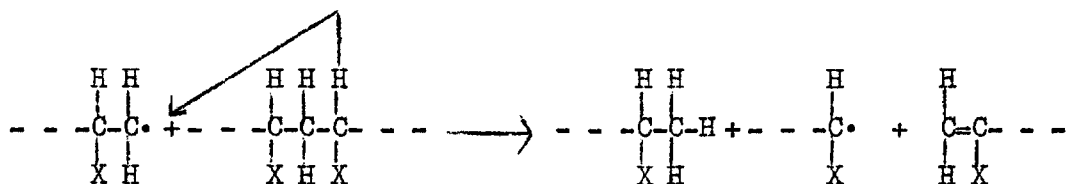


This represents the reverse of the propagation step in addition polymerisation and results in the formation of free monomer molecules.

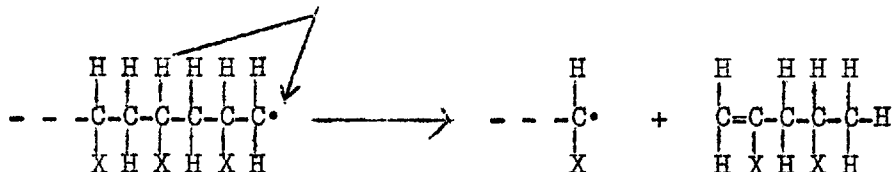
(iii) Free radical transfer

There are two ways in which this can occur.

Intermolecular transfer :



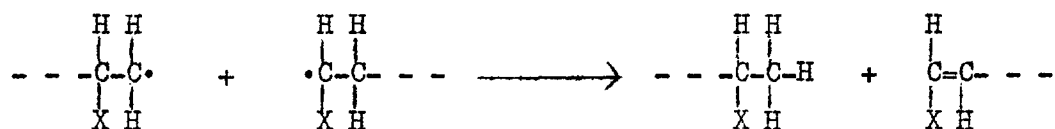
Intramolecular transfer :



Transfer involves the abstraction of hydrogen by the radical from its own or another molecule and is accompanied by fragmentation of the

carbon chain. In the case of intramolecular transfer the most probable point of attack is the third to the seventh carbon atom from the end of the chain.

(iv) Termination



Termination is thought to occur by the disproportionation of radicals, as above, or by the combination of radicals, the reverse of the initiation reaction.

In the reaction scheme outlined above, a free radical may react by one of two competing processes both of which involve bond scission. The first of these processes involves the 'unzipping' of radicals to yield monomer molecules; the second involves free radical transfer yielding chain fragments. Which of these processes predominates for a given polymer may be deduced by examining the experimental data. Table 3 shows for various polymers the monomer yield (expressed as the weight per cent of the pyrolysed part) and the zip length (23) which is a function of the chain length of the depolymerisation reaction.

These results may be interpreted in the following way. In the sequence polyethylene, polypropene, poly(2-methylpropene), polytetrafluoroethylene, monomer production increases with decreasing concentration of hydrogen in the carbon chain. Thus it appears that where less hydrogen is available for transfer the depropagation reaction becomes predominant. In the case of polystyrene, although the amount

Table 3

The thermal degradation of various organic polymers: monomer yields

Polymer of :	Monomer yield (weight per cent of volatile products)	Zip length (23)
Ethylene	0.025	0.01
Propene	0.2	-
Methyl acrylate	2.0	1.0
2-Methylpropene	20	3.1
Styrene	40	3.1
p-Methylstyrene	42	3.7
α -Deuterostyrene	70	11.8
α -Methylstyrene	>95	»200
Methyl methacrylate	>95	»200
Tetrafluoroethylene	>95	-

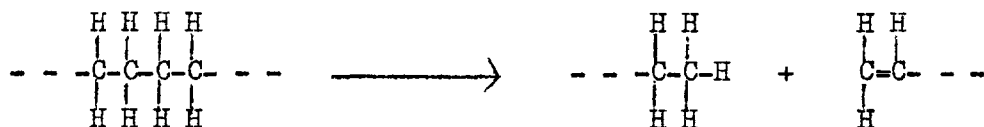
of hydrogen in the chain is the same as in the case of polypropene, presumably steric hindrance contributes to the predominance of the depropagation reaction. When the reactive tertiary hydrogen is replaced by a methyl group as in poly(α -methylstyrene), the further reduced hydrogen availability and increased steric hindrance increase the monomer yield to nearly 100 per cent. In the same way the structure of poly(methyl methacrylate) is consistent with the experimental results suggesting that the reaction proceeds almost entirely by depropagation.

Arguments of this nature lead to the conclusion that with polyethylene the extent of depropagation is negligible. The reaction is thought to proceed by random splitting of the polymer chain by radical transfer; this would lead to the complete spectrum of hydrocarbon fragments which has been observed as the reaction product. Random chain scission would obviously account for the sharp initial fall in molecular weight during the pyrolysis of polyethylene as compared with the more gradual fall in molecular weight which occurs during the degradation of poly(methyl methacrylate) to monomer (24).

The initially high rate of degradation of polyethylene found by both Madorsky (7) and Oakes and Richards (9) may be explained in terms of irregularities in the polymer structure. Thus oxygenated structures would encourage initiation and the tertiary hydrogen at points of branching of the carbon chain would be more reactive with respect to hydrogen abstraction than methylenic hydrogen. This interpretation is supported by the absence of a high initial rate during the degradation of pure polymethylene and the observation by Oakes and Richards (9)

that unsaturated groups of the type $\text{RCH=CHR}'$ and $\text{R}'\text{RC=CH}_2$ are formed only in the initial stages of the reaction.

An alternative mechanism for the degradation of polyethylene which does not involve radical formation has been proposed by Madorsky and Straus(13,25). It was suggested that, if free radicals were formed at all, it was difficult to see why so little unzipping to monomer took place. In the proposed scheme a thermal break in the chain occurs simultaneously with intramolecular hydrogen abstraction.



Thus, since no free radicals are formed, unzipping to yield monomer cannot occur. This is similar to a mechanism previously proposed for the degradation of polystyrene (26).

3. The influence of additives on the thermal degradation of polymers

A common property of many free radical chain reactions is the marked effect, often inhibitory, of small concentrations of certain additives. The use of this property as a diagnostic test for a free radical chain mechanism operating in organic polymer degradation is limited by the following factors. Suppose that the additive is initially incorporated in the polymeric material. Since degradation occurs with the polymer in the molten state, the accessibility of the additive molecules to the radical chain carriers may be restricted. Furthermore the proposed additive must have low volatility and high thermal stability to be effective at the high temperatures and low pressures used for the

investigation of degradation reactions. The latter requirement suggests that a polymer such as poly(methyl methacrylate), which undergoes degradation at a relatively low temperature, would be particularly suitable for an investigation of the effect of additives on polymer degradation. It has been reported for this polymer that, at temperatures in the range of 220-240°C, 1,4 diamino anthraquinone permanently inhibited the degradation as measured by production of the monomer (27). This was taken to confirm that the degradation proceeded by a chain mechanism with radical chain ends unzipping to form monomer and it was proposed that the reaction was suppressed by combination of inhibitor molecules with the chain end radicals.

Degradation of a polymer in a gaseous atmosphere containing a volatile additive reduces the experimental difficulties outlined above. Thus it might be expected that a gaseous additive would diffuse more readily throughout the reaction medium and hence offer the best possibility of influencing the course of the reaction. Such a study has been made using polytetrafluoroethylene at temperatures between 400 and 500°C (28). The rate of degradation, as measured by loss of weight, was found to depend on the nature of the gaseous atmosphere. Thus oxygen, nitric oxide, hydrogen sulphide and sulphur dioxide were found to increase the rate whereas chlorine, hydrogen, carbon tetrachloride and xylene were found to decrease the rate of degradation with respect to pyrolysis in nitrogen. It has been suggested that the inhibitor, for example chlorine, is effective by terminating the depropagation reaction to monomer and by participating in a chain

transfer reaction thus increasing the random fragmentation of the polymer chain (28). No work of this nature with polyethylene has been reported.

Examples of the inhibition of the degradation of hydrocarbon polymers include that of polystyrene by tetralin (29,30) and of polypropylene by aluminium silicate and xylene (31).

C The oxidation of hydrocarbons

1. General

Oxidation of polyethylene involves hydrocarbon molecules and despite the unique nature of long chain polymer molecules it seems probable that some of the reactions which occur will be similar to those taking place during the oxidation of simpler hydrocarbons. Indeed, because of the inherent difficulties in the study of polymer reactions, the interpretation of the mechanism has often been aided by analogy with those involving simpler molecules. In addition, when the oxidation of a polymer is severe, it is likely that low molecular weight hydrocarbons are produced so that an understanding of the mechanism of oxidation of volatile hydrocarbons will be of direct relevance. This section includes, therefore, a brief survey of the oxidation of simple hydrocarbon molecules which will aid the subsequent discussion of polymer oxidation. This survey is also necessary in order to appreciate the effect of additives on oxidation reactions. Following this survey is a discussion of polymer oxidation which is subdivided to reflect the two principal regions of interest. Studies in the low temperature region (below 200°C) have been made with a view

to understanding the processes involved in 'weathering', i.e. the deterioration of polymer properties produced by atmospheric oxidation, particularly in the presence of ultra-violet light. It is only recently that detailed studies have begun to be made on the other region of interest, namely that of oxidation at higher temperatures where the polymer burns.

As mentioned above there are many difficulties peculiar to the study of the oxidation reactions of polymers. One of these is that the reaction occurs between a gas and a liquid or solid so that for work to be kinetically meaningful precautions must be taken to avoid diffusion control. At relatively low temperatures it has been possible to produce films of such thickness that the reaction is not diffusion controlled (32). At higher temperatures, however, particularly those approaching the combustion region, there is a tendency for molten polymers to 'lump' which makes it extremely difficult to control sample thickness (32). Another difficulty arises from the size of the molecules involved. A vital step for the understanding of any mechanism is the identification of the reacting species. With polymers, however, the new groupings which appear as a result of the initial stages of oxygen attack form part of very large molecules and this makes the identification of such groups difficult. On the other hand, although volatile products where formed are identified relatively easily, such products are the result of a complex series of reactions and give no clue as to the initial mode of attack. Thus physical methods of analysis (oxygen uptake (33), infra-red analysis

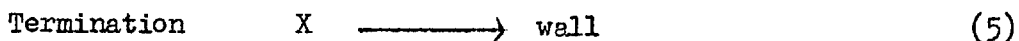
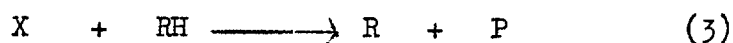
(32) etc.) are very important in the determination of the groupings formed.

2. The oxidation of volatile hydrocarbons

(a) Slow combustion

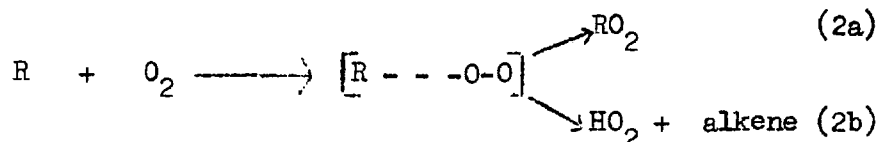
Mixtures of hydrocarbons with air or oxygen in the gas phase react at temperatures above about 200°C. The mechanism of these reactions at lower temperatures involves a free radical chain process in which the chain is propagated by reactive radical species and in which degenerate branching is caused by the slow further reactions of intermediate molecular products to give additional reactive radicals.

The reactions responsible for the oxidation of alkanes may be written in terms of the following general equations, where X represents any free radical and P represents molecules of product.

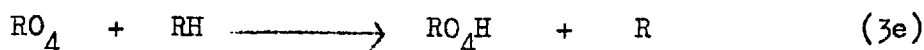
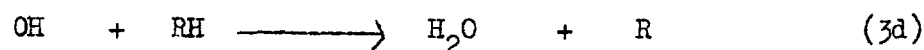
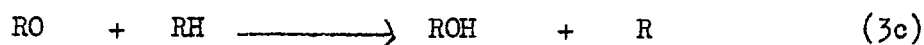
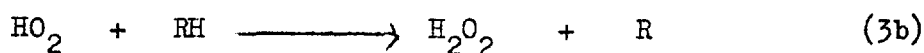


Each of the reactions written, however, consists of several alternative or concurrent steps. Thus in most alkane molecules there are carbon-hydrogen bonds of several, different molecular environments and the bond strengths of these differ appreciably (34). Several alkane radicals, R, will be formed in non-equivalent amounts (attack at tertiary hydrogen being the most strongly favoured) by the initiation

reaction (1) (35). Reaction (2), as represented, is also composite (36,37) :

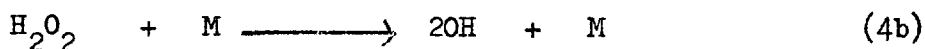
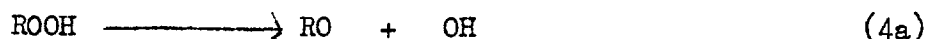


Reaction (3), the attack of the fuel molecule by free radicals, is perhaps the most composite of all :



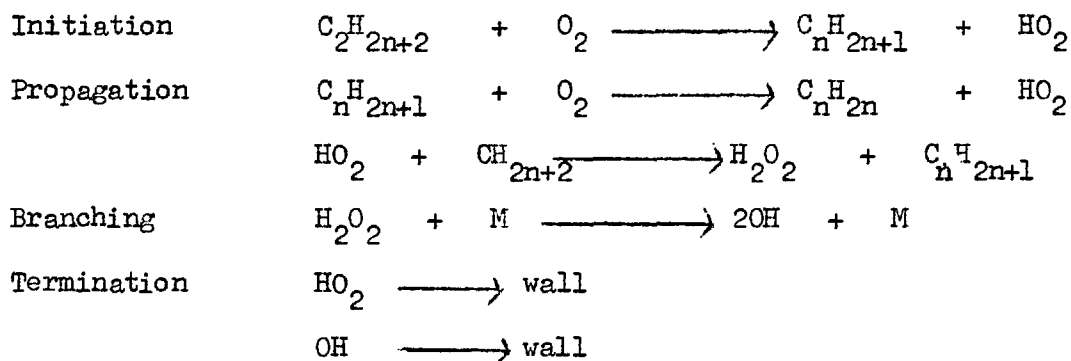
Thus the RO_2 and HO_2 radicals which are formed in (2a) and (2b) respectively may attack RH directly in (3a) and (3b) (37). Alternatively, however, RO_2 may isomerise and decompose to produce RO and OH (38,39,40) or isomerise and add on further oxygen to produce RO_4 (41); each of these new oxygenated radicals may then react with RH as in (3c,d,e) (42,43,44) to regenerate R and continue the chain. Reactions involving RO_2 may produce molecular products (38) (including alkenes, carbonyl compounds and epoxides).

Reaction (4), the branching step, includes the homolytic fission of peroxides (45,46,47,48) and the oxidation of aldehydes (49,50) :



Reaction (5) has not yet been fully investigated although the kinetic implications of the process have been elucidated (51, 52) and it is known experimentally (48,53) that the extent and nature of the surface present affect the rate of oxidation in a manner consistent with this theory.

At low temperatures (less than 200°C) the principal propagation and branching steps are (2a)(3a) and (4a) (45). At somewhat higher temperatures characteristic of cool flames, (2a), (3d), (3e), (4a) and (4c) tend to predominate. (38,54). At still higher temperatures (greater than 350°C) the reactions of importance are (2b), (3b) and (4b). At 400 to 600°C therefore, the primary steps involved in alkane oxidation may be written as follows (53).



This relatively simple reaction scheme by no means describes completely the whole course of oxidation. In the presence of an excess of oxygen, for example, intermediate products such as alkenes will be oxidised further.

Alkenes are oxidised in the gas phase by two major routes. Abstraction of hydrogen by free radicals from the allylic position leads to a mechanism analogous to that of alkane oxidation (55,56) in

which the primary products retain their unsaturated linkage to the fuel molecule. This is also similar to the predominant mechanism of the liquid phase oxidation of alkenes (57). Alternatively addition of radicals to the double bond leads to oxidation in which the unsaturated character is lost and produces carbonyl scission compounds and epoxides as the major products (58,59). Under conditions where alkenes are products of alkane oxidation, therefore, these further oxidation reactions may occur.

(b) Flames

Slow combustion, cool flames and the reactions preceding the ignition of hydrocarbon-oxygen mixtures may be studied under essentially isothermal conditions in a static system. The study of flames is obviously more complicated since the temperature, the flow of gases and the diffusion of reacting species vary according to the reaction co-ordinates. It is intended here to review the chemical rather than the physical characteristics of flames in order to provide a context in which the quenching of flames by additives may be discussed.

Flames studied in experimental work are of two general types. In premixed flames the reactants are mixed before burning and in diffusion flames they are not. Both systems can yield valuable results but although the conditions in diffusion flames approach more closely those existing in practice, premixed flames are perhaps the simplest for direct chemical study.

It has been known for some time that free radicals exist in

flames (60,61) and in the light of the detailed work which has since been reported the overall nature of flame propagation may be summarised as follows. As the fuel approaches the flame front it will be heated by conduction and radiation so that pyrolysis, to some extent catalysed by oxygen, will occur. On reaching a critical temperature a series of rapid free radical reactions occurs, some of which are highly exothermic and account for most of the heat released in the flame. Finally recombination reactions occur in the post-flame gases at a relatively low rate but with an accompanying heat release.

The nature of the reacting species and the products of the reaction have been determined by a number of techniques including spectroscopy and direct sampling. Relevant information has also been provided by experiments using flash photolysis and shock tubes.

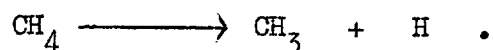
The most detailed study has concerned the hydrogen-oxygen flame and the similarity of the propagation and branching reactions observed to those occurring at lower temperatures in hydrogen-oxygen mixtures has aided the interpretation of the results. Much evidence opposes, however, the extrapolation of the mechanism of hydrocarbon oxidation at lower temperatures to flame temperatures. Thus some hydrocarbons which have the same burning velocities (62) are known to undergo oxidation at markedly different rates at temperatures around 500°C (63).

No general mechanism for the burning of hydrocarbons has yet been developed and detailed data have been obtained only for the simplest hydrocarbons. The nature and concentrations of reactants and products

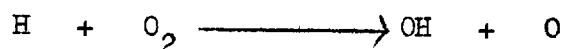
have been determined for a fuel-lean methane flame premixed with oxygen (64,65,66,67). As the fuel was consumed, hydrogen, water and carbon monoxide were rapidly formed with a subsequent decay of hydrogen and carbon monoxide concentrations as water and carbon dioxide were formed. Traces of formaldehyde were also observed. Studies of a diffusion flame of methane showed traces of acetylene, ethylene, ethane and methyl acetylene in the initial products (68).

A similar growth and decay of hydrogen and carbon monoxide to that in methane flames has been reported for premixed propane-air flames (69,70,71) and for ethane-air flames (72). Thus the evidence suggests that the last stage of the flames of simple hydrocarbons is a carbon monoxide-hydrogen-oxygen flame fed by the breakdown of the hydrocarbon.

Some of the reactions which have been suggested as occurring in a methane-oxygen flame are as follows. A concentration of radicals is established in the gas approaching the flame front by, for example, thermal and oxidative degradation of the fuel. Thus it is thought that the first stage in the thermal decomposition of methane in the temperature range 1000-2000°C is (73)

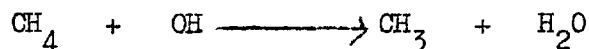


One of the important chain-branching reactions which may then occur is

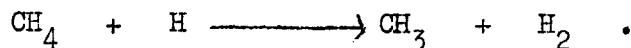


and it is thought that most of the oxygen is consumed by this reaction rather than by the attack of methyl radicals by oxygen molecules (74).

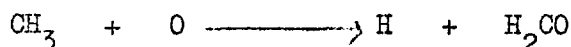
In fuel-lean mixtures the methane is thought to be consumed mainly by (65)



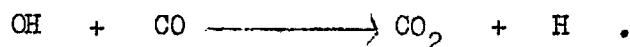
and in fuel-rich mixtures by (75)



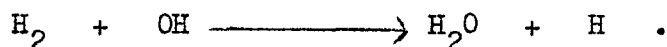
Carbon monoxide is probably formed via a reaction between methyl radicals and oxygen atoms although the primary product is uncertain(76). If the reaction is (75)



the presence of traces of formaldehyde would be explained, the latter compound subsequently reacting to form carbon monoxide. It has also been suggested (77) that formaldehyde takes part in a branching sequence of some significance. Carbon dioxide is thought to be formed from carbon monoxide (65) by the exothermic propagation reaction



Some of the water present must be formed from the initial product, hydrogen, by the reaction (65)



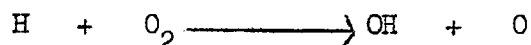
In fuel-rich premixed flames and in diffusion flames of methane the C_2 fragments observed (68) may be formed by radical combination reactions such as



Recent work (78) has related the consumption of ethane in fuel-lean ethane flames with the concentration of hydroxyl radicals and in fuel-rich flames with the concentration of hydrogen atoms and

it is supposed that the primary product of the initial reactions is the ethyl radical. In propane flames a mixture of C_1 , C_2 and C_3 hydrocarbon intermediates has been observed (70) although, significantly, no oxygenated hydrocarbon derivatives can be detected. Little further attempt has been made, however, to interpret the mechanism of combustion of ethane or of higher hydrocarbons.

It can be seen that the mechanism suggested for the oxidation of methane and presumably of other hydrocarbons in flames bears little relation to the mechanism which is thought to operate during slow combustion. This may be partly due to the fact that the rate of the branching reaction



increases more rapidly with temperature than the rate of the reaction



which is but little affected by temperature.

Now that an outline has been given of the types of reaction which occur characteristically in hydrocarbon flames an attempt will be made, in conclusion, to relate the stability of such flames to the reactions which occur. It is found that for a given fuel-oxygen mixture there is a critical flow velocity, the burning velocity, above which extinction occurs. Many factors probably contribute to the stability of the flame such as heat conduction to unchanged fuel gas (79) and diffusion of radicals against the flow of this gas (80). A more important consideration however is that of the balance between chain-breaking and chain-branching (81). The temperature of the fuel

mixture rises as it approaches the flame front. Eventually the 'ignition temperature' is reached at which the rate of chain-branching is equal to the rate of chain-breaking. Above this temperature the concentration of radicals rapidly increases until, at a 'critical' radical concentration, ignition occurs. There is thus an ignition lag corresponding to the time interval between the attainment of the ignition temperature and the instant of ignition. If the flow rate is such that there is insufficient time for the ignition lag to be completed before the gases have passed through the hot zone of the flame, the flame will be extinguished. Obviously additives which cause chain-breaking at the expense of chain-branching may interfere with this critical balance and cause flame quenching. The significance of this conclusion will be developed in greater detail in a subsequent section.

3. The oxidation of hydrocarbon polymers

(a) Low temperature oxidation

Work on the thermal oxidation of hydrocarbon polymers at low temperatures (below 200°C) has shown that the basic mechanism bears a close resemblance to that which occurs in other hydrocarbon systems (i.e. gas and liquid phase oxidation) in the same temperature range. The following survey is not intended to be comprehensive but is meant to emphasise the extent to which the polymers behave, during oxidation reactions, as typical hydrocarbons.

Infra-red spectroscopic analysis of polyethylene films during oxidation (82,83) shows that hydroperoxide groups are formed, the

concentration of which increases rapidly, after an initial induction period, to a maximum and thereafter remains constant or in some cases decreases. The concentration of carbonyl and hydroxyl groups increases throughout the oxidation even after the stage at which the hydroperoxide concentration reaches its maximum (83). At later stages of the oxidation the concentration of carboxyl and ester groups is also appreciable (83,84). The total unsaturation remains approximately constant throughout the reaction (83) although the nature of the unsaturated groups changes (82). The oxygen uptake is initially small but subsequently increases rapidly until a certain stage of the reaction and thereafter increases relatively slowly (33,84). The effect of increased branching of the polyethylene chain is to increase the initial rate of oxygen uptake (85) and the initial rate of formation of oxygenated groups (83,84) but not the limiting values of these quantities (84).

Changes in the molecular weight of polyethylene during oxidation are reflected in the nature of the solid obtained by cooling the sample at different stages of the reaction. Thus one worker reports that initially a wax-like solid was produced but eventually a hardening of the sample was observed (33). Experiments at over 200°C have shown the formation of volatile products which include carbon monoxide, carbon dioxide, formaldehyde, methane and ethylene (32).

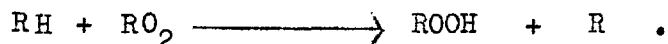
Experiments on polypropene (86) have shown the rate of oxidation (measured by oxygen uptake) to be approximately thirty times

greater than the rate of oxidation of polyethylene. Furthermore, for polypropene, the rate of formation of volatile products (which include water, hydrogen peroxide, acetone and aldehydes) increases as the hydroperoxide concentration decreases (87).

These results have led to the following generally accepted mechanism for the low temperature oxidation of hydrocarbon polymers. Initiation is thought to occur as a result of the formation of radicals at weak links or at irregularities in the carbon chain rather than by direct attack by oxygen (33). Once radicals have been formed the chain reaction leading to the formation of hydroperoxide groups (33) parallels that already outlined for the gaseous oxidation of hydrocarbons. The rate of this chain reaction will increase with the concentration of tertiary hydrogen on the chain; this may account for the observed effect of branching on the rate of oxidation (83), although the variation with polymer type of crystallinity or of ordered regions (in the melt) may also contribute to this effect (84).

The experimental data strongly suggest that hydroperoxides are the precursors for the formation of other oxygen containing groups. The hydroperoxide groups may either react to form more stable oxygenated structures or decompose to form reactive radicals, so that the development of the reaction rate exhibits features associated with degenerate branching (87). The formation of ketones does not involve chain scission whereas that of aldehydes does (84). Alcohols may be formed via the radicals produced by the decomposition of the hydroperoxide groups (88) and acids may result from oxidation of the aldehydes (84).

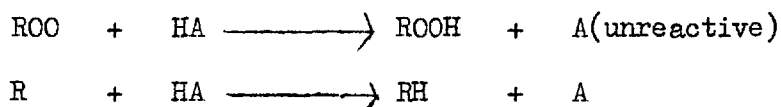
The reaction profile as measured by oxygen uptake is explained as follows. It is thought that the peroxides have a promoting effect on the reaction which is therefore autocatalytic (33,88). Thus, as the reaction proceeds, so the rate of oxygen uptake increases. Although in liquid phase oxidation such a reaction is homogeneously autocatalytic, it has been suggested that in polymer oxidation a peroxide group activates only adjacent sites on the polymer chain (33). Some workers suggest, however, that order in the polymer structure accounts for the initially low rate of oxidation (84). The final decrease in oxidation rate has been correlated (33) with crosslinking (possibly involving ether bridges) the occurrence of which has been deduced from the eventual hardening of the sample. It has been suggested that this reduces mobility in the polymer and hence the rate of the propagation reaction



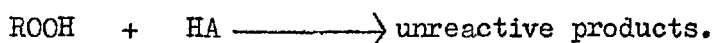
Other evidence, however, discounts crosslinking as the cause of the decrease in the rate of oxidation (89).

The low temperature oxidation of hydrocarbon polymers exhibits a typical property of radical chain reactions of sensitivity to small quantities of certain additives. Thus di-*p*-naphthyl *p*-phenylene diamine (which is used as an antioxidant during processing) causes a long induction period in the oxidation of polyethylene, after which the reaction proceeds at the normal rate (86). The nature of the chemical reaction which produces such an induction period depends on the nature of both the polymer and the additive. Two possible mechanisms have been suggested. The propagation cycle may be interrupted either by trapping

radicals (90) or by donation to chain-carrying radicals of labile hydrogen by the additive (91) by reactions of the type,



where HA is the additive. Alternatively the additive may decompose the hydroperoxide to give inactive products (92) thereby reducing chain-branching



These mechanisms have been discussed in a recent review of the effects of additives on the low temperature oxidation of polypropene (87).

(b) Burning

The widening application of polymeric materials has, in recent years, stimulated interest in the basic chemical mechanism by which such substances burn. No detailed work has yet been carried out in this field although some indirect evidence has emerged from experiments concerned with the inhibition of combustion. The following rather a priori discussion is made in the light of the small volume of experimental evidence which is available.

Some observations have been made on the burning of a polystyrene candle (93). On igniting the candle the pool of molten polymer was observed to be dark in colour, presumably due to the presence of carbon tars. As burning continued, however, a clear melt was obtained. Separate studies showed that pyrolysis of polystyrene in the presence of air produced brown pools of polymer whereas during pyrolysis in nitrogen no discolouration was observed. The temperature measured in the

sub-flame melt was between 230 and 540°C. Pyrolysis of polystyrene in the presence and absence of small quantities of air yielded essentially the same volatile products but no analysis was made of the pre-flame vapours of the burning candle.

The processes involved in the burning of a polymer may be envisaged as follows. The flame front conducts and radiates sufficient heat to raise the temperature of the polymer surface to that at which pyrolysis occurs. Thus volatile fuel is produced from the polymer to a large extent by a purely thermal degradation reaction, although some oxidative degradation may occur at the periphery of the flame.

For sustained combustion the rate at which fuel is fed to the flame must be equal to, or exceed, the rate of flame propagation. The flammability of a polymer will depend, therefore, on both its thermal stability and on the nature of the degradation products. The thermal stability of polyethylene is compared with that of polytetrafluoroethylene and a number of hydrocarbon polymers in table 4. With the exception of polytetrafluoroethylene, polyethylene appears to be the most thermally stable. All the hydrocarbon polymers yield volatile hydrocarbons on pyrolysis and are thus potentially highly combustible materials. The relation between the ease of combustion and the flammability of the products of pyrolysis is emphasised by the observation that polymers which pyrolyse to yield products which are not very flammable do not support combustion (95). These include polytetrafluoroethylene and poly(vinyl chloride) where the primary products of pyrolysis are tetrafluoroethylene and hydrogen chloride respectively.

Table 4
Relative thermal stability of polymer (94)

Polymer of :	k_{350}^*	T_h^{**} (°C)
Tetrafluoroethylene	2×10^{-6}	509
Ethylene	0.008	407
Propene	0.069	387
Styrene	0.24	364
2-Methylpropene	2.4	348
Methyl methacrylate	5.2	327
α -Methylstyrene	230	278

* k_{350} Rate of loss of weight of polymer expressed as per cent of residue per minute at 350°C

** T_h The temperature at which half the weight of the polymer sample volatilises on heating for 30 minutes.

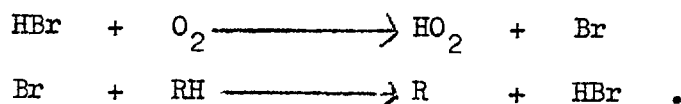
More work needs to be done before any further conclusions may be drawn. In particular analysis of the pre-flame vapours for a variety of polymers would show whether or not the fuel supplied to the flame results from a purely thermal degradative process.

D The effect of bromine-containing additives on the oxidation of hydrocarbons

1. The slow combustion of volatile hydrocarbons

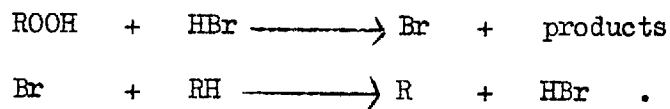
Hydrogen bromide is well known to promote the slow combustion of volatile hydrocarbons (96,97,98,99,100). Recent work on the slow combustion and spontaneous ignition of a number of fuels in the presence of organic bromides showed that unless the reaction took place under conditions where the additive decomposed to hydrogen bromide, no pronounced influence on the reaction was observed (101). The influence, where observed, for all the fuels studied (which included alcohols and aldehydes as well as hydrocarbons) was one of promotion on at least certain stages of the reaction. The later stages of the oxidation of methane at 510°C were, however, retarded by very small amounts of the additive.

Two possible ways in which hydrogen bromide may promote the oxidation of hydrocarbons are as follows. It may react with oxygen thereby providing an extra and more effective mode of chain initiation (101)



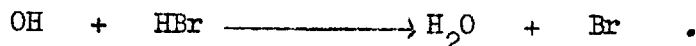
Alternatively it may react with intermediate peroxides and increase the

rate of chain branching (99)

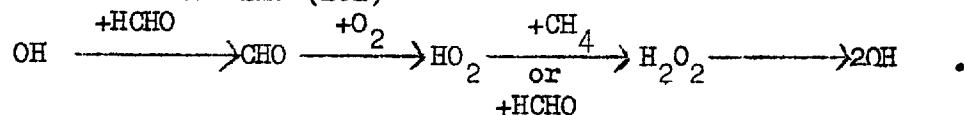


In order for the first mechanism to be effective, the direct reaction of hydrogen bromide with oxygen must occur more readily than attack of oxygen on the hydrocarbon. This is certainly the case with methane and promotion of the initial stages of oxidation is in fact observed (101). With formaldehyde, however, initiation by attack of oxygen on the fuel takes place more rapidly and it is of note that promotion by hydrogen bromide occurs only in the later stages of oxidation where the second mechanism suggested may operate (101).

The retardation of the later stages of oxidation of methane by hydrogen bromide has been ascribed to a reduction by the latter compound of the concentration of hydroxyl radicals



Since the normal fate of the bromine atom is to react with a fuel molecule to give an alkyl radical, the inhibition cannot be due simply to a reduction in the concentration of chain carriers. However, the reaction of formaldehyde (which is a product of the reaction) with hydroxyl radicals is thought to introduce a chain branching sequence which accounts, in the uninhibited reaction, for the increase in the rate of oxidation with time (101)



Since this branching sequence is unique in the case of methane, in that it involves formaldehyde, this interpretation of the retardation is

consistent with the observation that no similar effect was observed with higher hydrocarbons where formaldehyde is not the agent responsible for degenerate chain-branching.

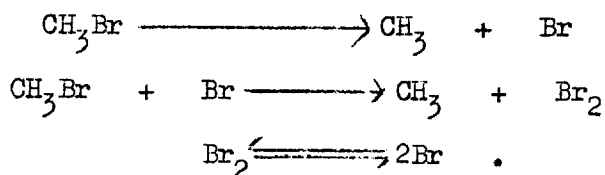
2. Flames of volatile hydrocarbons

Compounds containing halogen atoms, in particular bromine-containing compounds, are known to be effective inhibitors of hydrocarbon flame processes. Thus bromine-containing additives reduce the flammability limits (102,103), decrease the burning velocities (103,104,105,106) and increase the limit temperatures (103) of hydrocarbon-air flames. Bromine compounds are many times more effective, on a molar basis, than additives such as carbon dioxide and nitrogen (107) and this suggests that their effect is chemical in origin. Work on the inhibiting effect of brominated hydrocarbons, which is summarised below, strongly suggests that such molecules are precursors of the true inhibiting species which is thought to be hydrogen bromide.

A study of the effect of a number of bromomethanes on methane-air flame speeds (105) has shown that at the point of maximum flame speed (ten per cent by volume of fuel) their effect was equivalent to that of an equal quantity of bromine. A similar effect has been observed in a study of flammability limits (103). The effectiveness of hydrogen bromide in reducing flame speed varied little with variation of the composition of the fuel-air mixture whereas the effectiveness of other bromine-containing additives depended appreciably on the composition of the fuel-air mixture (105). It was concluded, for

bromine-containing additives other than bromine and hydrogen bromide, either that the decomposition of the additive was required prior to some critical stage of the combustion or that decomposition products other than hydrogen bromide and bromine were responsible for the inhibition. The correlation between efficiency and bromine content suggests that the former explanation is the more probable. Some work on methane-air diffusion flames inhibited by bromomethane (108) has suggested that the molecule, rather than its decomposition products, is the effective inhibiting species but no convincing mechanism, based on this suggestion, has been advanced.

The mechanism of the inhibition of hydrocarbon flames by brominated hydrocarbons which is generally accepted at the present time (77,105) is illustrated by the particular case of bromomethane in a methane-air flame. As the flame front is approached, thermal decomposition of bromomethane, catalysed by bromine atoms, occurs

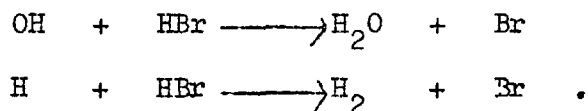


Hydrogen bromide is then produced by reaction of bromine atoms with fuel molecules



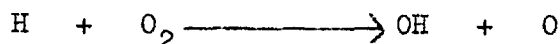
In addition, it is known that hydrogen bromide is one of the most abundant products of the slow combustion of bromomethane (109) so that hydrogen bromide will also be produced by such a process early in the flame. Now it is known that hydrogen bromide is sufficiently

stable at the temperatures encountered in the reaction zone of the flame (about 2000°K) to exist mainly as undissociated molecules during its residence time in that zone (105). Thus the concentration of certain active radicals may be reduced by reaction with hydrogen bromide

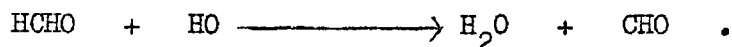


This interpretation is consistent with the observation that, as the concentration of brominated hydrocarbon was increased, both the flame speed and the concentration of excited hydroxyl radicals were reduced (105).

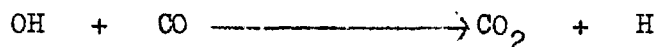
It was concluded in section C.2(b) that one of the most important factors controlling flame stability was the balance between branching and termination reactions in the hot zone of the flame. Such a balance would be disturbed as a result of the replacement by bromine atoms of radicals participating in the branching reaction



and in the reaction



The latter reaction, which has been discussed previously, may lead to branching. The rate of the exothermic propagation reaction



would also be reduced. It must be pointed out, however, that the production of bromine atoms does not imply a reduction in the rate of the propagation reaction since the normal fate of bromine atoms is to react with the fuel



In conclusion, it can be seen from this suggested mechanism of inhibition that the effectiveness of an inhibitor depends on its ability to produce an inhibiting species which is not so unstable as to decompose before it reaches the required reaction zone of the flame but is sufficiently reactive to react when it reaches that zone.

3. Burning polymers

Attempts to reduce the flammability of hydrocarbon polymers have involved two general methods of approach. In the first an additive is mixed physically with the polymer (110) and, in the second, substances are incorporated chemically in the polymer structure either by copolymerisation or by direct replacement of groups on the polymer chain (111). Both methods have proved to be effective, although the following discussion will concentrate on the former method.

The discovery of effective inhibitors of polymer combustion has relied on defect tests of flammability since no fundamental work on the causes of such inhibition has been reported. There is no uniformity in the flammability tests used by various investigators but as an example of these, the following is perhaps the most commonly used (112). The additive is mixed with the polymer by milling or by dissolving the polymer and additive in a volatile solvent and flashing off the solvent. The resultant material is cut into standard strips which are held in a flame until they ignite. Materials which do not ignite are called 'non-burning'; those which ignite in the flame but will not support combustion when the source of ignition is removed are termed 'self-

extinguishing'. The relative effectiveness of additives as inhibitors may be determined by comparing the times taken for the burning samples containing them to be extinguished after the source of ignition has been removed.

The quenching of the combustion of hydrocarbon polymers by halogen-containing compounds has been known for some time and the use of organic bromine compounds in particular has been described frequently in the patent literature (110,112). A few general comments may be made on the relative effectiveness of organic bromides as inhibitors. The most effective bromine compounds appear to be those with bromine attached to an aliphatic or cycloaliphatic structure (113). Those containing bromine attached to aromatic carbon atoms are much less effective. The influence of a given additive also depends, however, on the polymer to which it is added. Thus three per cent by weight of ammonium bromide in polystyrene produces a self-extinguishing material whereas concentrations of up to six per cent of this additive are insufficient to stop polyethylene burning(95).

A considerable advance was made in this field when it was discovered that the incorporation into the polymer of certain free radical initiators in conjunction with an organic bromide substantially reduced the quantity of the latter compound necessary to produce self-extinction (114,115). Dicumyl peroxide, for example, which fulfills the essential requirement of being stable under the conditions encountered during polymer processing, has been shown to be such a synergist. Thus 0.25 per cent by weight of dicumyl peroxide in

polystyrene reduced the quantity of acetylene tetrabromide necessary to cause self-extinction from 5 to 0.5 per cent (115).

The work described above may give only indirect information regarding the inhibition mechanism. In an attempt to approach the problem more fundamentally, two critical stages in the polymer burning process which may be influenced by additives must be considered.

(i) The additive may react with the polymer in the condensed phase in such a way as to decrease the rate of pyrolysis of the polymer thereby reducing the rate at which fuel is supplied to the flame to such an extent that the flame is extinguished. Alternatively the additive may modify the pyrolysis reaction by changing the nature of the products.

(ii) The additive may release a species in the flame itself which reduces the rate of certain free radical reactions essential to flame propagation thus causing quenching of the flame.

No conclusive evidence for either mechanism has yet been reported. However, the following experimental evidence may be of some importance. Hydrogen bromide has been shown to be an effective quenching agent when added to either the fuel side or the oxygen side of diffusion flames of styrene and benzaldehyde (93) which are known to be major products of the thermal and oxidative degradation of polystyrene. The concentration of hydrogen bromide in the initial products of pyrolysis of polystyrene (in which bromine containing additives were incorporated) was found to be about 7 per cent (by volume) for pyrolysis in nitrogen and more than 20 per cent for pyrolysis in air (93). The greater the

effectiveness of the additive as a flame quenching agent the greater was found to be the concentration of hydrogen bromide in the initial pyrolysis products of the modified polystyrene. The observation that the incorporation of hydrogen bromide into the air side of diffusion flames was more effective in causing quenching than its incorporation into the fuel side, suggested that the region in the periphery of the flame of a burning polymer might be critical.

Whether the critical phase for the inhibition is the pyrolysing polymer or the flame, it appears probable that it is a species derived from the additive, rather than the additive itself, which is the active agent. This assumption requires that the stability of the additive should be such that it decomposes either in the pyrolysing polymer or in the flame. The observation that a given additive may be effective for one polymer but not for another may simply reflect a difference in the pyrolysis temperatures of the polymers.

The effect of free radical initiators in enhancing the effect of additives is not understood. It has been suggested that the synergist may promote combination of the polymer with bromine thereby ensuring that the degradation of the polymer and the release of an inhibiting species occur simultaneously (114). Alternatively the free radical initiator may catalyse the production of hydrogen bromide followed by inhibition of the flame by the latter compound (93).

This survey has shown how much fundamental work needs to be done, particularly with polyethylene, before a mechanism of flame-quenching of polymers by bromine additives can be postulated.

E The present work

All the preceding sections have been concerned with chemical topics of supposed relevance to the phenomenon of burning hydrocarbon polymers. From this survey it is obvious that no fundamental investigation has yet been made of the mechanism by which such polymers burn nor of the mechanism by which certain additives inhibit this combustion. It appears, however, that the most promising class of inhibitors is that of organic bromides and a possible scheme for investigating the inhibition of combustion of a given polymer by such compounds would be:

(i) to determine the nature of the fuel supplied to the flame when the polymer burns;

(ii) to determine the effect of adding a variety of bromine compounds to the flame of a fuel mixture comparable with that supplied to the flame of the burning polymer;

(iii) to investigate the effect of a variety of bromine compounds on both the thermal and oxidative degradation reactions of the polymer.

In this work it was decided to tackle the problem described in (iii) above both for its chemical interest and for its relevance to the general study of the inhibition of the combustion of hydrocarbon polymers. The polymer chosen as the subject for this study, namely polyethylene, is formally the simplest hydrocarbon polymer. It was proposed in this initial investigation to add hydrogen bromide and various simple volatile organic bromides to the atmosphere surrounding the degrading polymer since gaseous additives diffuse more readily throughout the reaction

medium than small quantities of solid additives incorporated into the polymer. It was thought that such investigations would show what effect, if any, the nature of the surrounding atmosphere has on the thermal and oxidative degradation of polyethylene. It was also hoped to discover whether any observed inhibiting influence could be attributed to particular chemical species. Information on these points should help to elucidate the factors controlling the flammability of hydrocarbon polymers.

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A Apparatus

1. The reaction vessel system

The reaction vessel system and the apparatus for the introduction of solid samples into the reaction vessel are shown in figure 4. The cylindrical reaction vessel, R, made of pyrex glass, was 9 cm. long and 7 cm. in diameter. Entry to the reaction vessel was made via a horizontal pyrex glass tube, I, 2 cm. in diameter. The lower, semicircular half of this tube projected 7 cm. into the reaction vessel to form a platform, P, which had a vertical lip of glass, L, at its end. The tube, which was 46 cm. long from the point where it entered the reaction vessel to the other end, could be closed by insertion of a ground-glass stopper into the socket, C. The tube projected horizontally 28 cm. outside the furnace, F, and was connected to the vacuum line by 2 mm. capillary tubing through the tap T.

A double rail, D, (two parallel lengths of pyrex rod joined together at each end) ran the whole length of the introduction tube from the vertical lip, L, to the socket, C. A glass peg, A, on the end of the rail, which fitted into a depression, B, in the introduction tube, held the rail in position when in use. The rail could easily be removed for cleaning.

The introduction rod, E, sketched in figure 4, was made of silica with a cradle, C, at one end and a piece of soft iron, M, sealed into the other. The introduction rod had a total length of 28 cm. The cradle held a flat-sided silica boat, 30 mm. long, 10 mm. wide and 10 mm. deep (internal dimensions 28 mm. long, 8 mm. wide, 9 mm. deep),

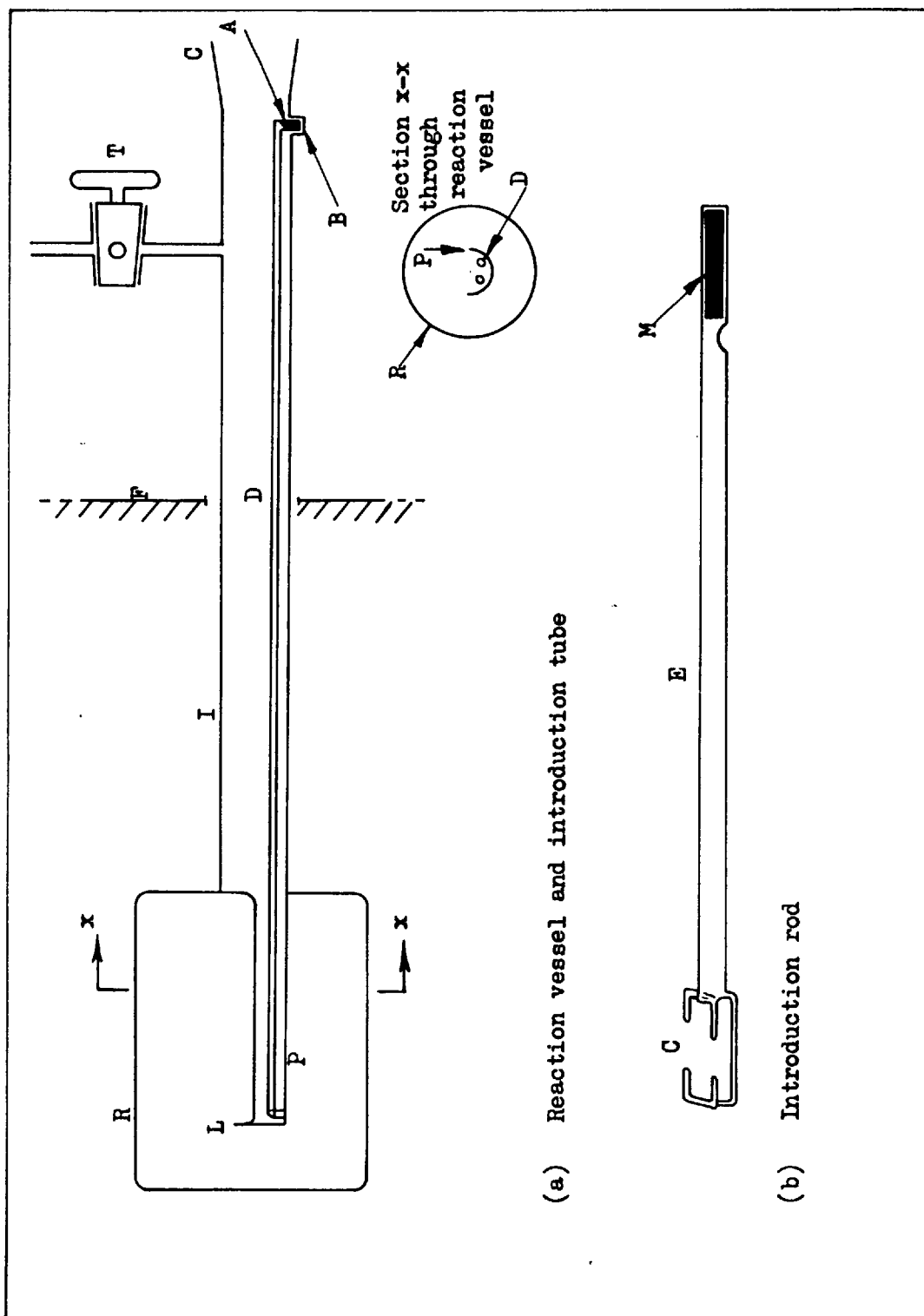
Key to figure 4(a)

A	Peg on guide rail
B	Depression in tube
C	Socket
D	Guide rail
F	Furnace
I	Introduction tube
L	Vertical lip
P	Platform
R	Reaction vessel
T	2 mm. capillary tap

Key to figure 4(b)

C	Cradle for boat
E	Introduction rod
M	Soft iron

Figure 4



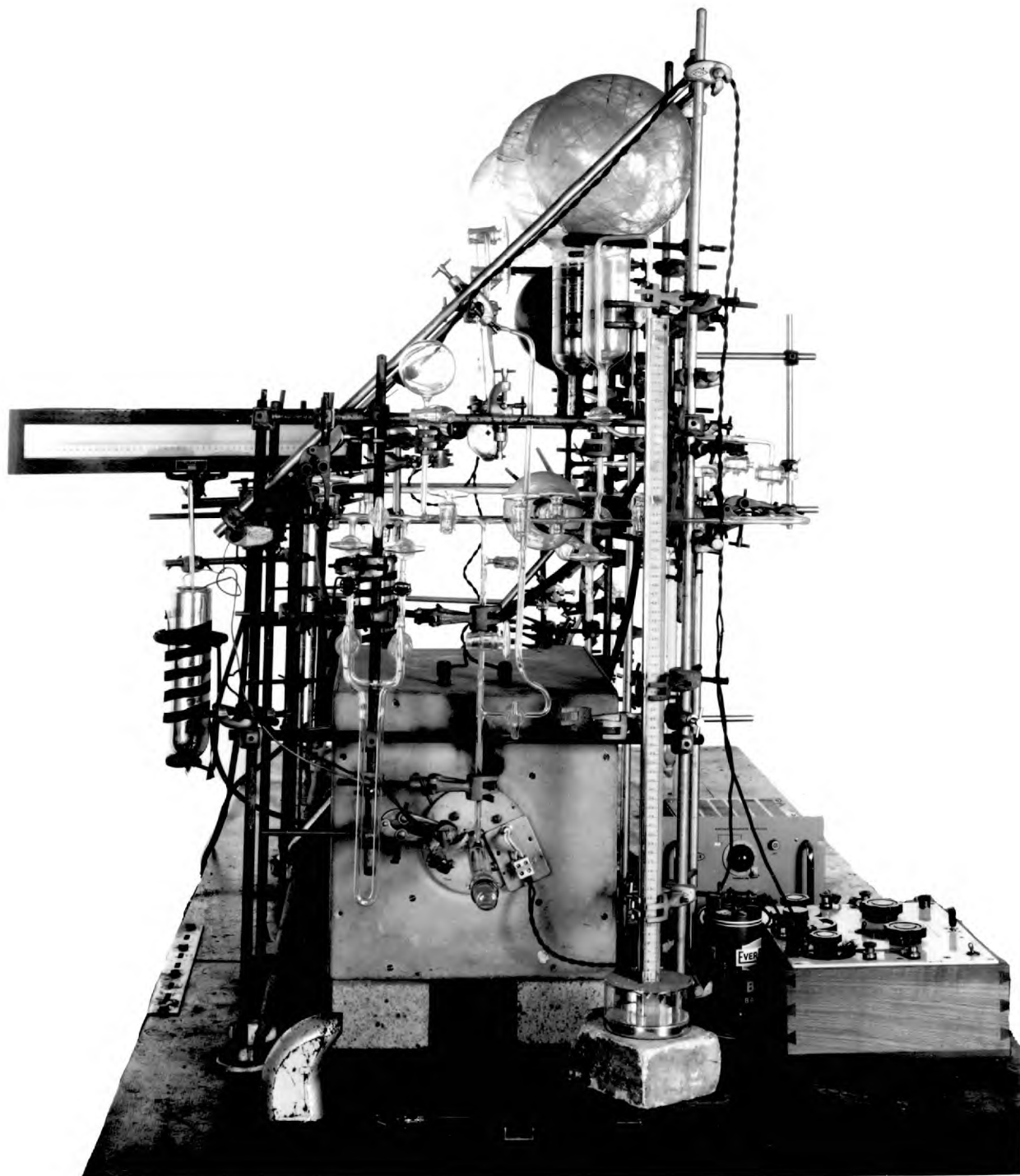
Reaction vessel and apparatus for the introduction of polyethylene samples

so that, when the rod containing the boat was placed in the introduction tube, the lower, horizontal part of the cradle fitted between the rails and the boat rested on top of them. The rod and boat could be placed in the introduction tube so that they were completely outside the furnace even when the ground-glass stopper was inserted into the end of the tube. Then with the reaction vessel under vacuum, or containing a prepared gaseous atmosphere, the rod (which had a piece of soft iron in its end) could be pulled into the furnace by a powerful magnet held outside the introduction tube. The boat could then be brought to rest on the platform in the reaction vessel with the end of the cradle just touching the vertical lip, L, at the end of the platform.

2. The vacuum line

A front view of the apparatus is shown in plate 1 and the lay-out of the apparatus is shown schematically in figure 5. Figure 5(b) shows the vacuum line and the position of the reaction vessel, R, but not the connection of the reaction vessel system to the vacuum line. This is shown in figure 5(a) together with the spiral gauge, A, which was mounted above the vacuum line.

The reaction vessel was placed horizontally in the electric furnace, F. It was connected by 2 mm. capillary tubing to a mercury manometer, M, a premixing vessel, P (volume 540 cm^3), and a standard volume vessel, V (135 cm^3). A 10 cm^3 bulb, C, was used for the introduction into the system of the vapours of volatile liquids. At B, two ball joints were fitted to the line by 2 mm. capillary tubing which fitted into the sockets of a U-tube used for taking samples of volatile products for analysis. S_1 , S_2 and S_3 are 5-litre pyrex globes for the

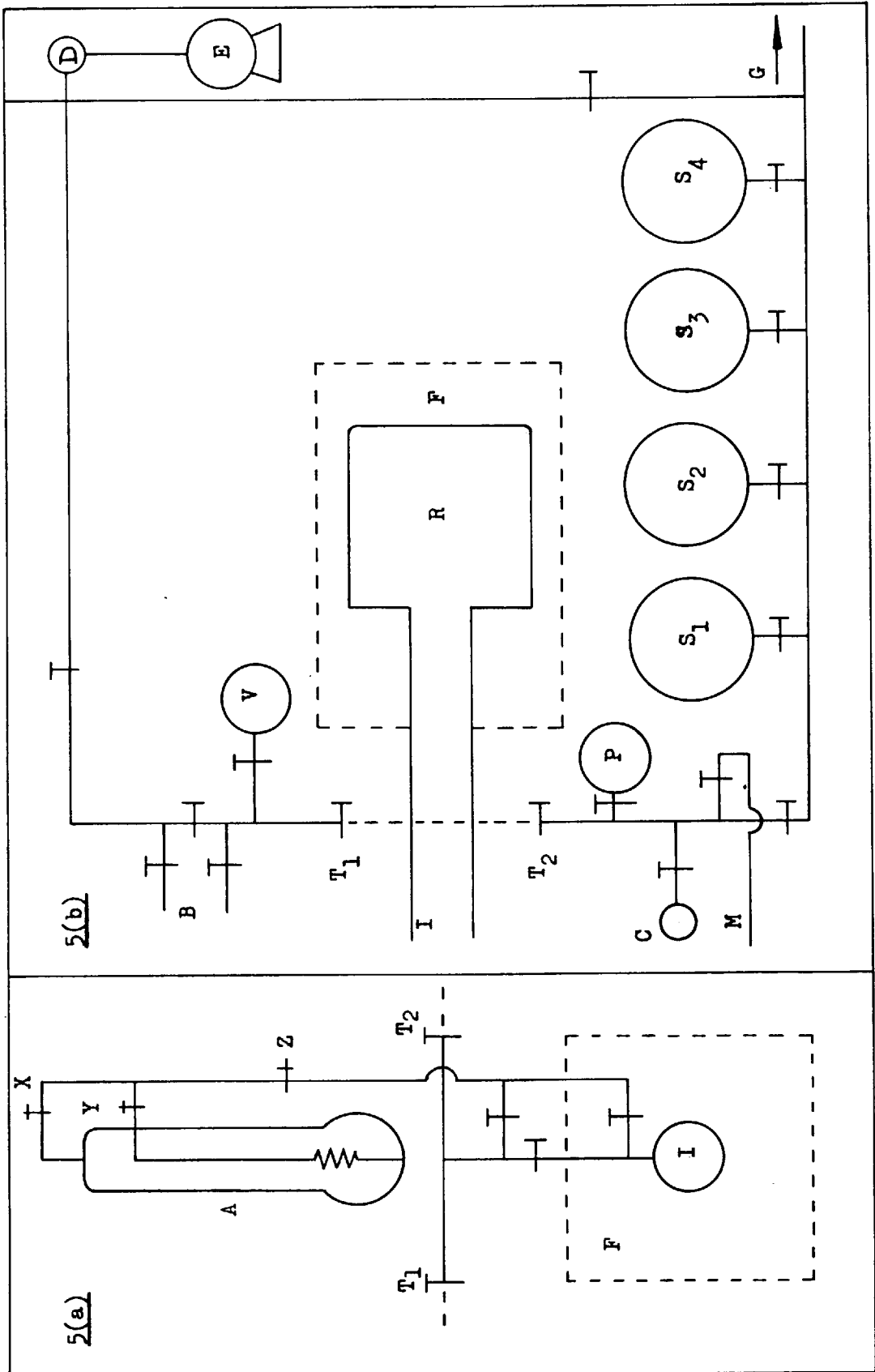
Plate 1The apparatus

Key to figure 5(a)

A	Spiral pressure gauge
F	Furnace
I	Introduction tube (cross-sectioned)
T_1, T_2	Taps
X	Tap to outer chamber
Y	Tap to spiral
Z	Tap to line

Key to figure 5(b)

B	Ball joint connections for product sampling system
C	10 cm. ³ globe for volatile liquids
D	Mercury diffusion pump
E	Rotary oil pump
F	Furnace (as in 5(a))
G	Gas introduction system
I	Introduction tube (as in 5(a))
M	Mercury manometer
P	Premixing vessel
R	Reaction vessel
S_1, S_2, S_3	5-litre storage globes
S_4	2.5-litre storage globe
T_1, T_2	Taps (as in 5(a))
V	Standard volume vessel



storage of oxygen, nitrogen and helium respectively and S_4 is a 2.5-litre globe for the storage of hydrogen bromide. The gas introduction system, G, which is not shown in figure 5(b), consisted of two traps, a magnesium perchlorate drying column and a mercury manometer.

The pumping unit consisted of a mercury diffusion pump, D, backed by a rotary oil pump, E, which provided a vacuum of about 10^{-5} mm. Hg. throughout the apparatus. Traps were inserted between the oil pump and the diffusion pump and also between the diffusion pump and the apparatus. When the system was operating these traps were cooled in liquid nitrogen in order to prevent organic products entering either of the pumps and to assist in obtaining a good vacuum.

The taps and joints in the vacuum line were lubricated with Kel-F 90 Grease as this was found to be resistant to hydrogen bromide.

3. The furnace system

The furnace was constructed of welded metal and the outer casing was made of Sendanyo sheeting. The heating element consisted of nichrome wire (total resistance 49 ohms) wound on a vitreosil tube (length 30 cm., internal diameter 11.5 cm.) and covered with asbestos cement. The tube was also lined with a thick copper sheath to provide a more uniform temperature distribution along the length of the furnace. The entrance to the furnace tube was closed with a thick Sendanyo 'plug'. The furnace was connected through an ammeter, the temperature controller and a switch to the 230 V. A.C. mains.

The temperature of the furnace was measured by a spot-welded chromel-alumel thermocouple which was periodically calibrated against a standard platinum-rhodium thermocouple. The leads to the hot junction

were enclosed in a twin-bore mullite tube. The hot junction was placed in the furnace level with the position of the middle of the boat when the latter was in position during a run. The cold junction, enclosed in a glass sheath, was placed in melting ice. The e.m.f. developed was measured by a potentiometer, capable of reading to 0.01 mV.

Temperature control of the furnace was provided by a proportional temperature controller (A.E.I. no. RT3R/MK2). The controller was in two parts, an input unit and a voltage-stabilised power regulator. The input unit contained an input bridge, an amplifier, a phase-sensitive detector and an electronic power supply. The input bridge was a Wheatstone bridge circuit, one arm of which was a platinum resistance thermometer (resistance 10 ohms) placed in the furnace and another arm of which was the temperature-setting control. The input unit delivered a D.C. current signal to the power regulator proportional to the magnitude of the temperature deviation from the set value. The control allowed temperature settings graded by about 0.15 C° in the temperature region in which it was used. The unit gave good control of temperature both in constancy and in speed of temperature change for small changes in setting. The latter was necessary on account of the procedure used during some of the experiments. For a given setting the temperature fluctuation over a period of three hours (which was the longest duration of any of the experiments performed) was less than ± 0.2 C°.

A preliminary measurement was made of the distribution of the furnace temperature along its length so that the reaction vessel could

be placed over a length where the temperature was substantially constant. Then with the reaction vessel in the selected position the temperature distribution over the length of the reaction vessel was measured by a thermocouple introduced along the inside of the introduction tube. The measured temperature distribution is shown in figure 6. It was found that, with the furnace thermocouple reading 430°C , the distribution over the length of the reaction vessel occupied by the boat when the latter was in position was $\pm 0.25^{\circ}\text{C}$ and the temperature distribution over the total length of the reaction vessel was $\pm 3^{\circ}\text{C}$.

4. The spiral gauge

A glass spiral gauge (A, figure 5(a)) was used in conjunction with a lamp and scale for the measurement of pressure change during studies of the oxidation of polyethylene. A calibration curve (deflection of light versus pressure increase in mm.Hg.) was used to convert the actual readings to known pressure units. This was checked periodically. The optical system of the spiral gauge was such that a pressure change of 1 mm.Hg. gave a deflection of about 8 mm. on the cm. scale.

B Materials

1. Polyethylene

The polyethylene used in these investigations was commercial polyethylene supplied by the Dow Chemical Company. Information concerning the polymer is given in table 5. It was originally supplied as small pellets, each weighing 25-30 mg.

For the work involving the thermal degradation of the polymer,

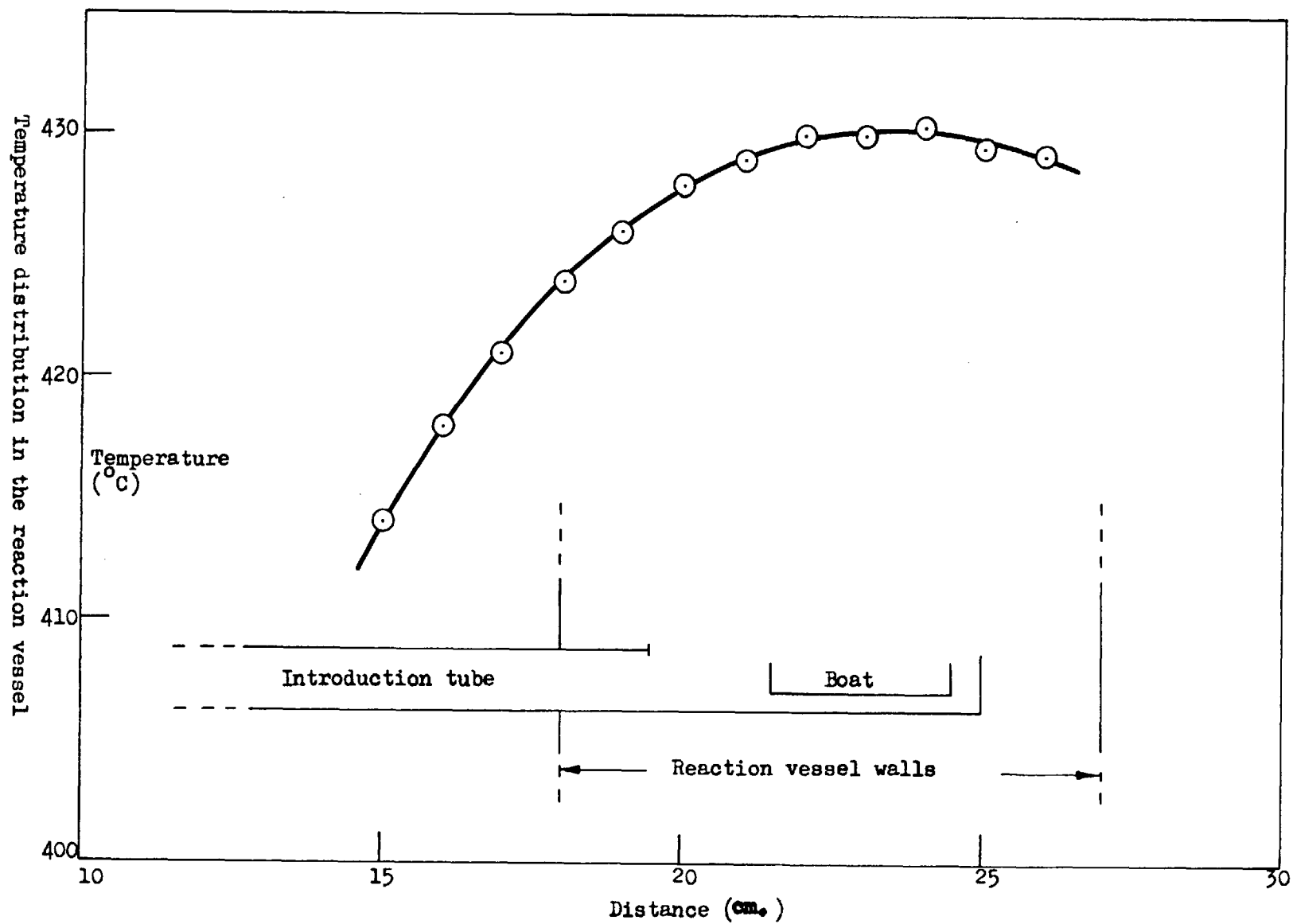


Figure 6

Table 5

Some properties of the polyethylene used

Density (gm. cm. ⁻³)	0.914
Softening point (°C)	31
Stabilizer content (ppm) *	87
Viscosity average molecular weight	30,000
Unsaturation (C=C per 1000 C atoms)	
Trans	0.05
Vinyl	0.06
Vinylidene	0.54
Carbonyl (per 1000 C atoms)	
Ester	0.007
Ketone	0.012
Methyl groups (per 1000 C atoms)	28.3

* Stabiliser: 2,6-di-t-butyl-4-methylphenol

the samples to be pyrolysed were obtained as follows. Very thin slices were cut from the pellets by means of a razor blade. These slices were further subdivided so that each particle of polymer obtained weighed between 0.1 and 0.2 mg.

For all the work involving the oxidative degradation of the polymer, the polyethylene was used in the form of a powder which was prepared in the following way. About 0.2 gm. of the polymer was dissolved in 80 cm³ of AnalaR xylene at 80°C and the resulting solution was slowly poured into 250 cm³ of methanol when the polymer was precipitated as a white solid (which presumably no longer contained any stabiliser). When all the solution had been added to the methanol, the polymer was allowed to settle and the bulk of the supernatant liquid was decanted off. Fresh methanol was then added with vigorous stirring, in order to break up the polymer (which coalesced on precipitation) thereby ensuring complete penetration of the methanol. The polymer was filtered off and washed with methanol and the excess alcohol was roughly squeezed out by pressing between filter papers. The powdered polymer was then placed on a watch glass and allowed to dry slowly in air. When it had dried sufficiently (after about 6 hours), the polymer was ground on the watch glass using a glass spatula until it formed a very fine powder. Finally it was dried by heating in an oven at 80°C for 24 hours. Sufficient powdered polymer was prepared in this way to ensure that samples from the same batch were used in all oxidation experiments.

2. Oxygen, nitrogen and helium

These gases were obtained from cylinders and dried by passage over magnesium perchlorate. The oxygen was condensed in a liquid nitrogen trap and the middle fraction was allowed to evaporate into the storage vessel. 'Oxygen free' nitrogen (British Oxygen Co.) was used throughout the work and was passed slowly through two cold traps immersed in liquid nitrogen into the storage vessel. Helium was used from a cylinder without further purification.

3. Additives

(a) Hydrogen bromide

Hydrogen bromide was, in the early stages of this work, prepared by the action of bromine on tetralin (tetrahydronaphthalene) (116). Bromine was slowly added dropwise to the tetralin through which nitrogen was bubbled at a steady rate. All traces of moisture had been removed from the system before the bromine was added by sweeping out with dry nitrogen for half an hour. Any bromine or tetralin vapour carried over by the hydrogen bromide was removed by bubbling consecutively through a bubbler filled with tetralin and a U-tube immersed in ice-salt. The hydrogen bromide was finally condensed in a trap immersed in liquid oxygen on the vacuum line. When sufficient hydrogen bromide had been collected, the liquid oxygen trap was isolated and the nitrogen was pumped off. The middle fraction of the condensate was then allowed to vaporise into a blackened 2.5-litre storage globe.

Later in the work it was possible to obtain hydrogen bromide directly from a cylinder (supplied by The Matheson Co.) The compound was condensed in a trap, containing phosphorus pentoxide on glass wool, immersed in liquid nitrogen. The middle fraction was distilled into a storage globe. Some of the previous runs which had been carried out with hydrogen bromide prepared by bromination of tetralin were repeated using the hydrogen bromide from a cylinder; in all cases identical results were obtained.

(b) Organic bromides

The purest available commercial samples of organic bromides were carefully redistilled before use.

(c) Hydrocarbons

Pentane and pent-1-ene were also obtained commercially and were purified by careful fractionation. Propene was obtained from a cylinder without further purification.

C Procedure

1. Temperature measurements

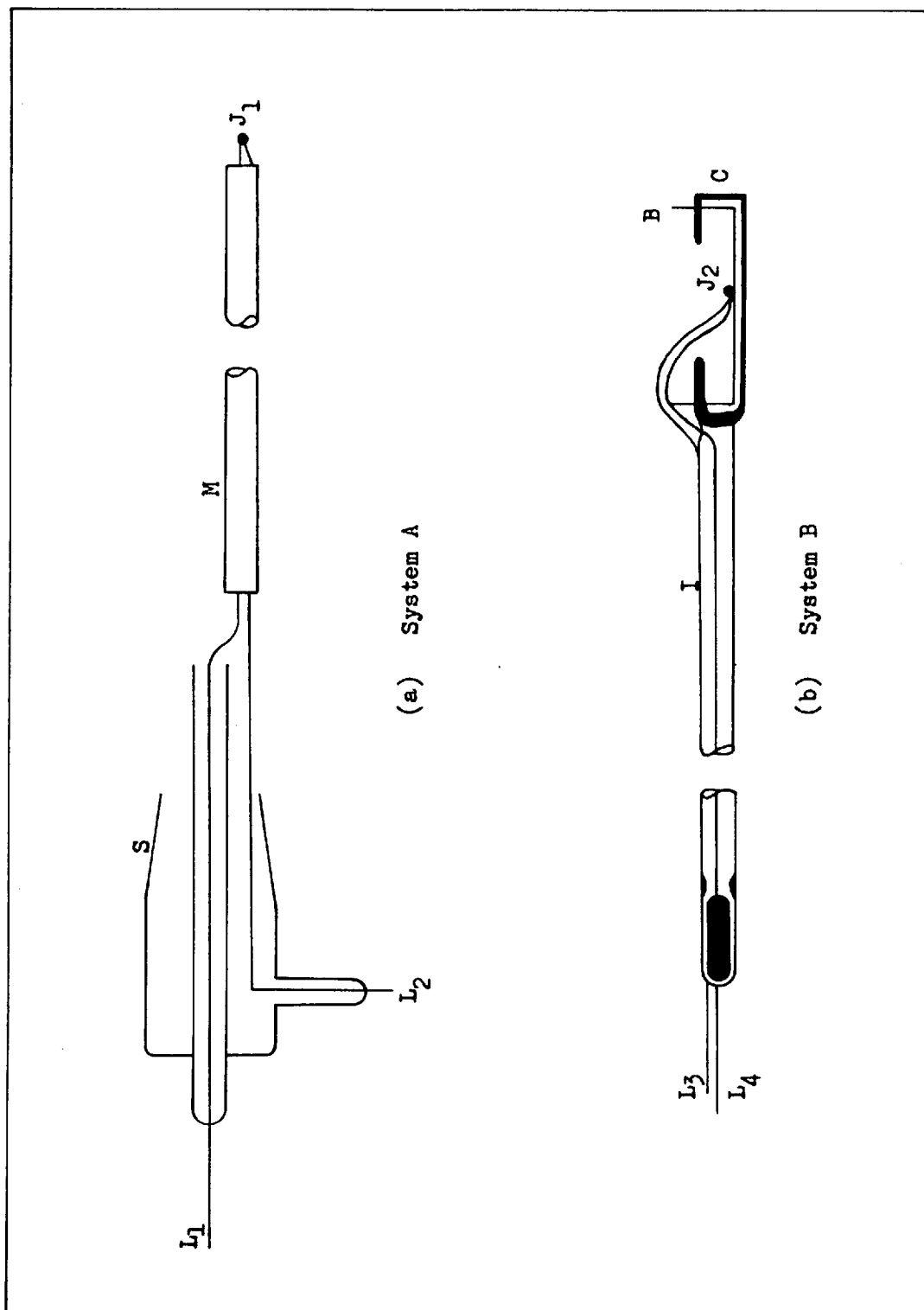
These experiments were designed (i) to investigate the influence of different gaseous atmospheres in the reaction vessel on the rate of temperature rise of a cold object placed in it; (ii) to determine the time taken, from the introduction of the boat into the reaction vessel for it to reach the temperature of the furnace, using a system which approximated as closely as possible to that used during the pyrolysis experiments.

For the first of these investigations system A (figure 7(a)) was

Key to figure 7

B	Silica Boat
C	Cradle on introduction rod
I	Introduction rod
L_{1-4}	Thermocouple leads
J_1, J_2	Thermocouple junctions
M	Twin-bore mullite tube
S	Cone

Figure 7



Apparatus used in temperature measurements

used and for the second investigation system B (figure 7(b)) was used. Both systems employed chromel-alumel thermocouples previously calibrated against a platinum-rhodium thermocouple over the required temperature range. In both cases the thermocouple leads were sealed into pyrex glass tubes which in turn were sealed into a ground-glass cone as shown in figure 7(a). In system A the thermocouple leads were then enclosed in a twin-bore mullite tube whereas in system B the leads ran along the side of the introduction rod to the junction which was in contact with the bottom of the silica boat. The distance in each case from the cone to the thermocouple junction was such that when the thermocouple was placed in the introduction tube so that the cone sealed the end of the tube, the thermocouple junction occupied a position in the reaction vessel equivalent to that occupied by the middle of the boat during the pyrolysis experiments. The procedure used for all experiments, using systems A and B, was as follows. The system was introduced into the reaction vessel so that the cone sealed the end of the introduction tube. The reaction vessel was then evacuated by pumping for exactly one minute after which time the required gaseous atmosphere was introduced. The temperature of the thermocouple junction was then determined at given time intervals until a constant temperature was registered by the thermocouple junction.

2. Pyrolysis experiments

(a) Loss of weight measurements

The polymer sample was weighed in the silica boat. Considerable care was needed with the small sample size (5 mg.) used in the majority of experiments since the balance used was scaled to give

readings to 0.1 mg. Consistency in weighing to this order was good, however, as it was found that the weight of a boat was the same to within 0.1 mg. when it was weighed before each experiment during a given series of runs.

The boat was then placed in the cradle of the introduction rod and the rod placed in the part of the introduction tube external to the furnace. The introduction tube was sealed and the system was evacuated until a good vacuum (ca. 10^{-5} mm.Hg.) was indicated by applying an H.F. Tester Coil to the vacuum line.

While the reaction vessel was being pumped out the appropriate gas or gas mixture was introduced into the premixing vessel, P. The sharing factor between the reaction vessel, R, and the premixing vessel had been accurately determined over a wide range of gas pressures (with the rod and boat in the furnace) and at the temperatures used in the experiments. Thus, if the pressure in P before sharing was known, that developed in P and R after sharing could be readily calculated. These calibration experiments were carried out using nitrogen.

The boat and introduction rod were then drawn into the reaction vessel by the magnet and the stopwatch was started as soon as the boat was in position. The gaseous atmosphere was immediately introduced, the tap on the premixing vessel being closed as soon as the pressure was steady.

The temperature of the reaction vessel had been pre-set before the introduction of the sample to 2.5°C above the temperature required for the experiment. After the sample had been in the reaction vessel for four minutes, the setting on the temperature controller was reduced

to that required for the experiment. It was found that, by using such a procedure, a steady temperature in the furnace was attained in the minimum possible time.

After pyrolysis for the required time, the sample was withdrawn, the reaction vessel was evacuated, and cold air was blown onto the part of the introduction tube containing the boat in order to accelerate cooling. Five minutes after the boat had been withdrawn, air was admitted to the reaction vessel, the stopper was taken from the end of the introduction tube, the vacuum grease was removed from the socket and the boat and introduction rod were withdrawn. The boat was then weighed.

After each run the guide rail was removed and cleaned. The inside of that part of the introduction tube situated outside the furnace was wiped with a Kleenex pad moistened with trichlorethylene to remove condensed product. The guide rail was replaced, the introduction tube was sealed, and oxygen was admitted to the reaction vessel to oxidise completely any products condensed inside the reaction vessel. The reaction vessel was then evacuated prior to the next run until a good vacuum was obtained.

The residue of polymer in the silica boat was removed using a nickel spatula. Any fragments of polymer remaining were removed by heating the boat in a closed crucible for five minutes.

At intervals the reaction vessel was removed from the line and placed overnight in a furnace at 500°C. This was done to remove the charred product which was found to accumulate on a 3-4 cm. length of the inside of the introduction tube just inside the furnace.

(b) Product sampling

After pyrolysis had taken place for the required time, the reaction vessel was shared for 30 seconds with an evacuated U-tube immersed in liquid nitrogen. The reaction vessel was then evacuated slowly through the U-tube for another 30 seconds. This was done with the sample still in the reaction vessel and the time of sampling was taken as that when pumping through the trap commenced. Under experimental conditions where the yield of volatile product was small the run was repeated and the sample was added to that of the first run in order to obtain a sufficient quantity of volatile product for a reasonable quantitative estimation.

3. Oxidation experiments

(a) General procedure

The polymer sample was weighed in the silica boat, the rod and boat were introduced into the introduction tube and the system was evacuated. When a good vacuum had been obtained the rod and boat were introduced into the reaction vessel and the sample was pyrolysed under vacuum (with pumping to remove products) for exactly 10 minutes, at which time the oxygen or oxygen-additive mixture was introduced.

(b) Pressure increase measurements

The spiral gauge was used to measure the pressure increase in the system during oxidation and it was also used as the premixing vessel throughout all oxidation experiments.

Oxygen was admitted to the reaction vessel after the polymer had undergone pyrolysis under vacuum for exactly ten minutes by opening tap Z with taps X and Y open (figure 5(a)). Five seconds after the

introduction of oxygen, tap X leading to the spiral was closed. The pressure increase was then followed on the centimeter scale, the first reading being taken 15 seconds after the introduction of the oxygen. In this way it was possible to obtain a comparison of the pressure change in the reaction vessel, shared with the outer chamber of the spiral gauge, with the pressure in the system after five seconds' oxidation. The pressure increase during the first five seconds of oxidation was obtained as follows.

The pressure of oxygen in the system at zero time (i.e. the instant at which the oxygen was introduced) was known to ± 0.5 mm. from the sharing ratio between the spiral gauge and the reaction vessel. On completion of the run the pressure of gas in the outer chamber was reduced by about 2 mm. at a time, from a pressure of 20 mm. greater, to a pressure of 20 mm. less than the pressure of gas which was in the system at zero time. Readings were taken for each pressure reduction on the scale of the spiral gauge and on the mercury monometer. A graph was then plotted of the manometer reading against the reading on the scale of the spiral gauge, and the scale reading was determined appropriate to the monometer reading for the pressure of gas in the system at zero time. This scale reading gave the pressure increase in the system after five seconds' oxidation. The pressure increase after five seconds was added to the values obtained during the experiment to give absolute pressure changes with respect to the pressure of gas in the system at zero time.

(c) Loss of weight measurements

Using the spiral gauge as the premixing vessel, oxygen was

introduced to the system after the polymer had undergone pyrolysis for ten minutes in a vacuum. The tap to the spiral gauge was left open during oxidation so that the experiments would be consistent with the pressure increase measurements. After oxidation for a given time interval, the tap to the premixing vessel was closed, the polymer sample was withdrawn and at the same instant the reaction vessel was evacuated. The outer tube in the region of the boat was cooled by blowing cold air onto it. When the rod and boat were cold they were removed and the boat was weighed.

(d) Product sampling

After oxidation for a given time interval, the tap to the spiral gauge was closed and the reaction vessel was shared for five seconds with a globe, of volume 540 cm.³, which had previously been evacuated. For analysis of residual oxygen this globe was shared with the evacuated U-tube and the oxygen was determined. For analysis of volatile hydrocarbons and oxygenates the sampling U-tube was immersed in liquid nitrogen and shared for five minutes with the globe containing the products. The globe was then evacuated through the U-tube so that any products left in it would condense in the tube. No products were found to have diffused into the spiral gauge during the experiments.

The relative number of moles of a gas shared between the reaction vessel and the globe was determined from the sharing ratio between the two, and confirmed by sharing a sample of pentane between them and determining the quantity in each by gas chromatography. Thus, after the number of moles of a given product in the globe after sharing

had been determined the number of moles of that product present in the reaction vessel at the instant of sharing could be calculated.

D Analytical methods

1. Gas-liquid chromatography

An apparatus manufactured by the Shandon Scientific Co. Ltd. was used for most of the product analysis work done. A complete description of this apparatus and the preparation and calibration of the columns has been given previously (117).

Throughout the work double U-tubes were used for sampling. These enabled the air to be swept clear of the connecting arms of the tubes and by-pass prior to the introduction of the sample onto the column. This was particularly important where analysis was being carried out for residual oxygen.

A propylene carbonate/squalene column in series with a silicone oil column (No. 1) was used for the estimation of hydrocarbons, carbon dioxide, bromomethane and bromoethane. A di-2-cyanoethyl ether column (No. 2) was used for the estimation of low molecular weight organic oxygenates. The specifications of both columns are given in table 6. For the major hydrocarbon products determined using column 1 a plot of the detector response to the substances against their heats of combustion is shown in figure 8. The sensitivity calibrations of the system for those hydrocarbons which were not determined directly were deduced from this curve. The values of the detector response for carbon dioxide, bromomethane and bromoethane (analysed on column 1) are given in table 7 and the values for the oxygenates (analysed using

Table 6

Gas-liquid chromatography specifications

Carrier gas : 75% hydrogen + 25% nitrogenDetector : hydrogen flame

	Column used for	
	Analysis of hydrocarbons (column 1)	Analysis of oxygenates (column 2)
Length (ft.)	19.5 (a) + 4.5 (b)	12
Inlet pressure (cm. Hg.)	220	231
Outlet pressure (cm. Hg.)	76	76
Flow rate (cc. min ⁻¹)	47	50
Temperature (°C)	35.5	80
Packing	(a) 27.25% propylene carbonate + 2.75% squalene on 60-100 mesh acid washed embacel. (b) 30% MS 550 silicone oil on 60-100 mesh acid washed embacel.	40% di-2-cyanoethyl ether + 0.01% squalene on Chromosorb -P

Figure 8

Detector response for hydrocarbons separated on Column 1 as a function of their heats of combustion

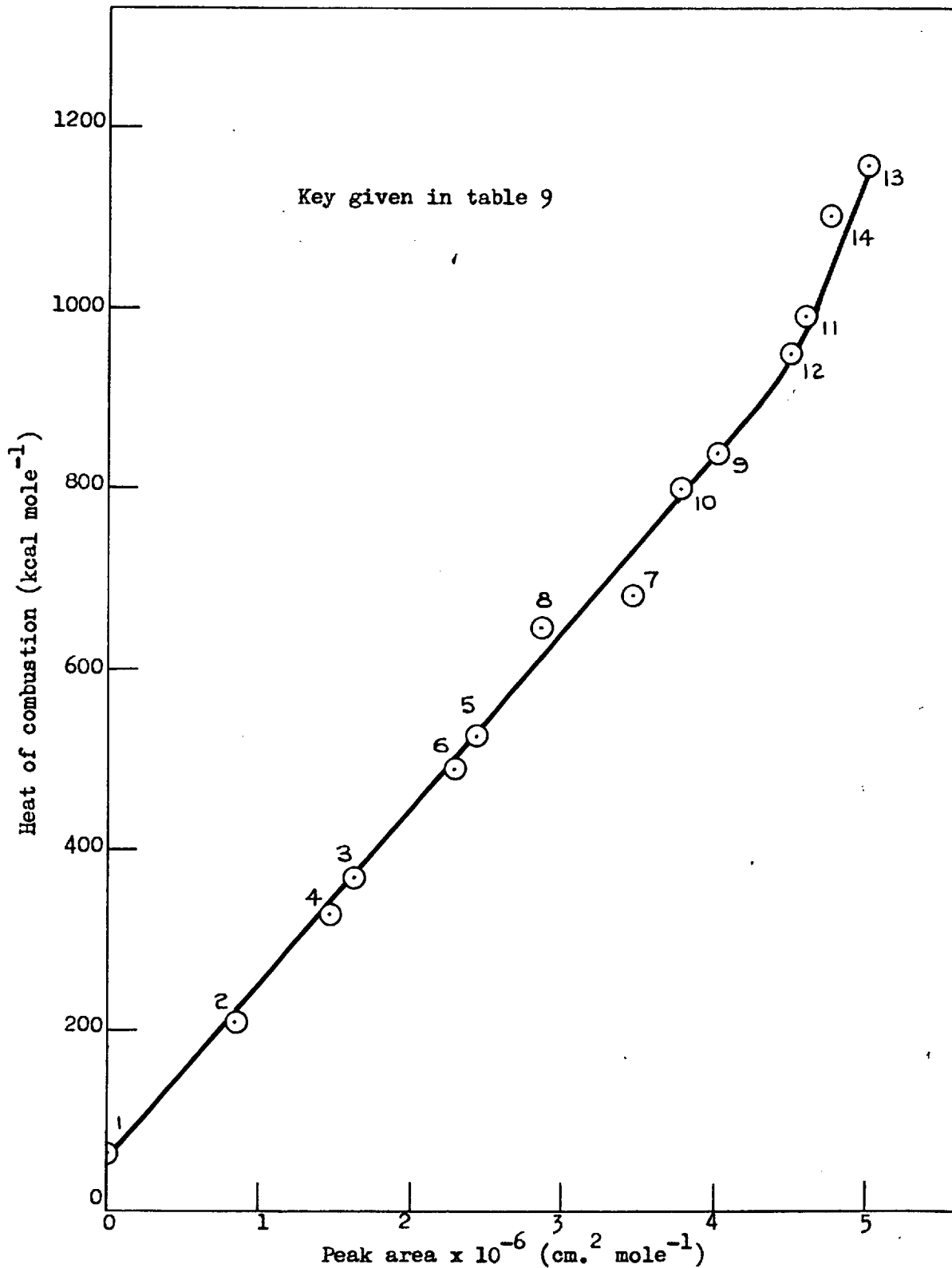


Table 7

Response of the detection system to substances separated on
column 1

Substance	Sensitivity $\times 10^{-6}$ ($\text{cm}^2 \text{ mole}^{-1}$)
Carbon dioxide	0.47
Bromomethane	0.55
Bromoethane	1.10

column 2) encountered in analysis work are given in table 8. Values for the retention times are given in table 9.

A third column was prepared specifically for the analysis of organic bromides which might be formed during both thermal and oxidative degradation of polyethylene in the presence of hydrogen bromide. The results of these experiments were such that no detailed work on this column was necessary. Thus only the essential details of this column, which has been fully described in the literature (118), will be given here. The column was packed with a mixture of 90 per cent by weight silicone oil and 10 per cent Tween 60 (polyoxyethylene sorbitan monostearate) on crushed firebrick sieved to 40 to 60 mesh (40 gm. of stationary phase to 100 mg. of firebrick). This column was used in conjunction with a Perkin Elmer Fractometer (Model 451), fitted with a hot-wire detector. Helium was used as the carrier gas and the column temperature was 80°C. A wide variety of organic bromides could be separated on this column (118). The retention times for the largest substituted hydrocarbons investigated (the monobromopentanes) were reasonable and the sensitivity of the system to bromoalkanes was of the order of $10^5 \text{ cm}^2 \text{ mole}^{-1}$.

2. Elemental Microanalysis.

Samples of the polyethylene residue after degradation in the presence of hydrogen bromide were analysed for carbon, hydrogen and bromine by the Microanalytical Laboratory of the Chemistry Department of Imperial College.

Table 8

Response of the detection system to oxygenates separated on column 2

Substance	Sensitivity $\times 10^{-6}$ ($\text{cm}^2 \text{ mole}^{-1}$)
Propanal	0.9
Acetone	1.9
Butanone	2.9

Table 9

Retention times of substances separated on columns 1 and 2

Column 1			Column 2	
Substance	Key to fig. 8	Retention time(min.)	Substance	Retention time(min.)
75% H_2 + 25% N_2	1	-	Acetone	19.4
Methane	2	2.7	Propanal	27.4
Ethane	3	2.9	Butanone	34.0
Ethylene	4	2.9		
Propane	5	3.8		
Propene	6	4.2		
Butane	7	6.0		
But-1-ene	8	7.0		
But-2-ene(trans)	-	8.1		
But-2-ene(cis)	-	9.2		
Pentane	9	11.8		
Pent-1-ene	10	13.7		
Pent-2-ene(trans)	-	15.8		
Pent-2-ene(cis)	-	17.3		
Hexane	11	26.7		
Hex-1-ene	12	31.4		
Hex-2-ene(trans)	-	35.4		
Heptane	13	64.4		
Hept-1-ene	14	75.3		
Carbon dioxide	-	3.4		
Bromomethane	-	12.5		
Bromoethane	-	28.7		

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A Preliminary investigations

1. Influence of the surrounding gas on heat transfer in the reaction vessel

The temperature of the hot junction of a chromel-alumel thermocouple, arranged as in system A (figure 7) was measured as a function of time when the reaction vessel contained helium, nitrogen and hydrogen bromide respectively (figure 9). In the case of nitrogen the rate of temperature increase was determined with the reaction vessel containing 100, 200 and 400 mm. of gas. The curves obtained for these three pressures of nitrogen were identical. Similarly variation of the pressure of helium in the range 100 to 400 mm. was found to have no effect on the rate of temperature increase.

The rate of temperature rise was found to be appreciably dependent on the nature of the gas in the reaction vessel and followed the order helium > nitrogen > hydrogen bromide. An experiment was also carried out with 50 mm. of bromoethane in the reaction vessel. The curve was intermediate between those of nitrogen and hydrogen bromide.

2. The time taken for the boat to attain the furnace temperature

In these experiments the thermocouple junction was arranged as in system B (figure 7). Some results obtained when the reaction vessel contained helium, nitrogen and a nitrogen + hydrogen bromide mixture are shown in figure 10. The rate of rise of temperature of the thermocouple junction was greater in the helium than in the nitrogen atmosphere. No difference could be detected in the rates of temperature rise for atmospheres of pure nitrogen and a nitrogen +

Figure 9

Influence of surrounding atmosphere on the rate of temperature rise of a thermocouple junction (system A)

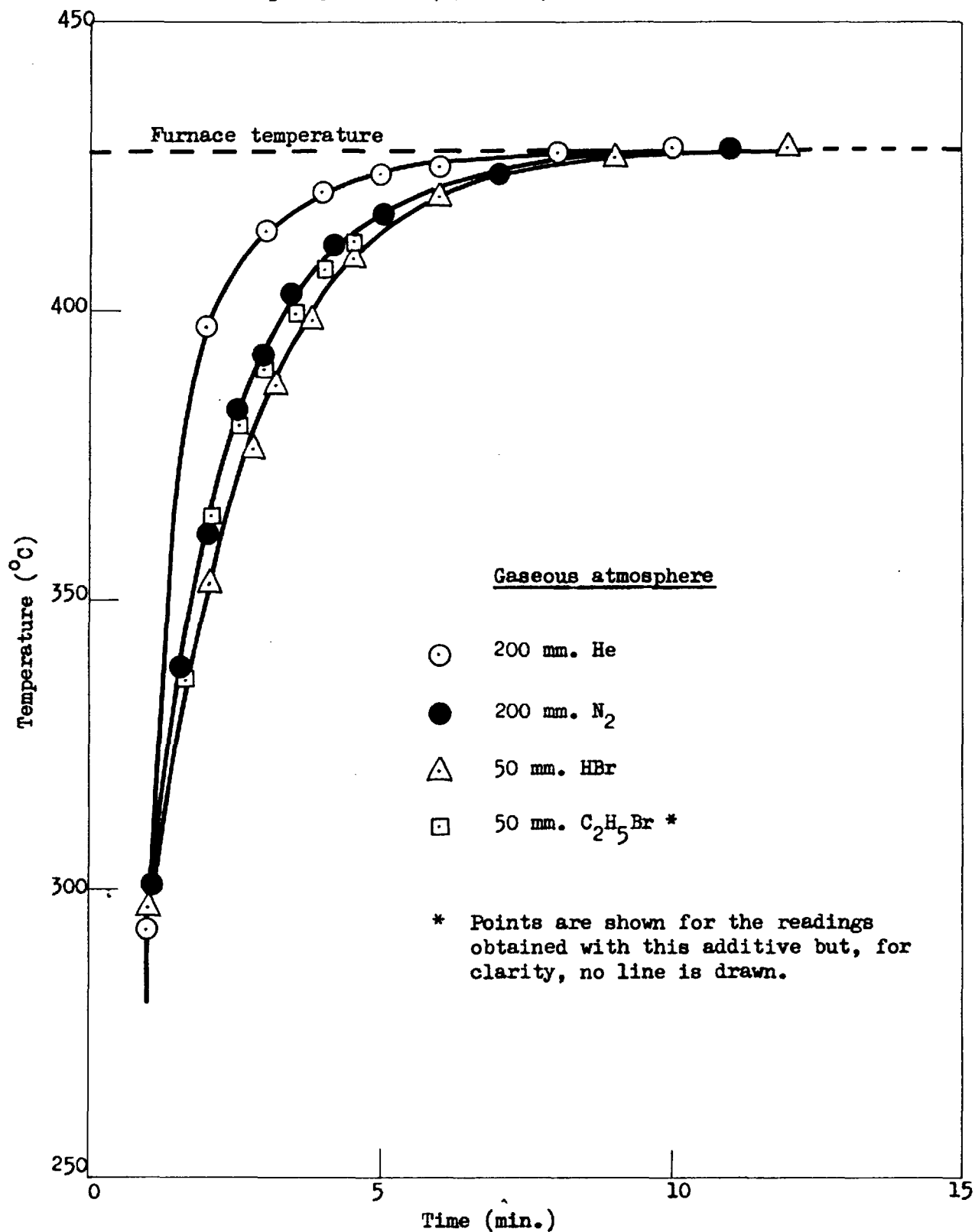
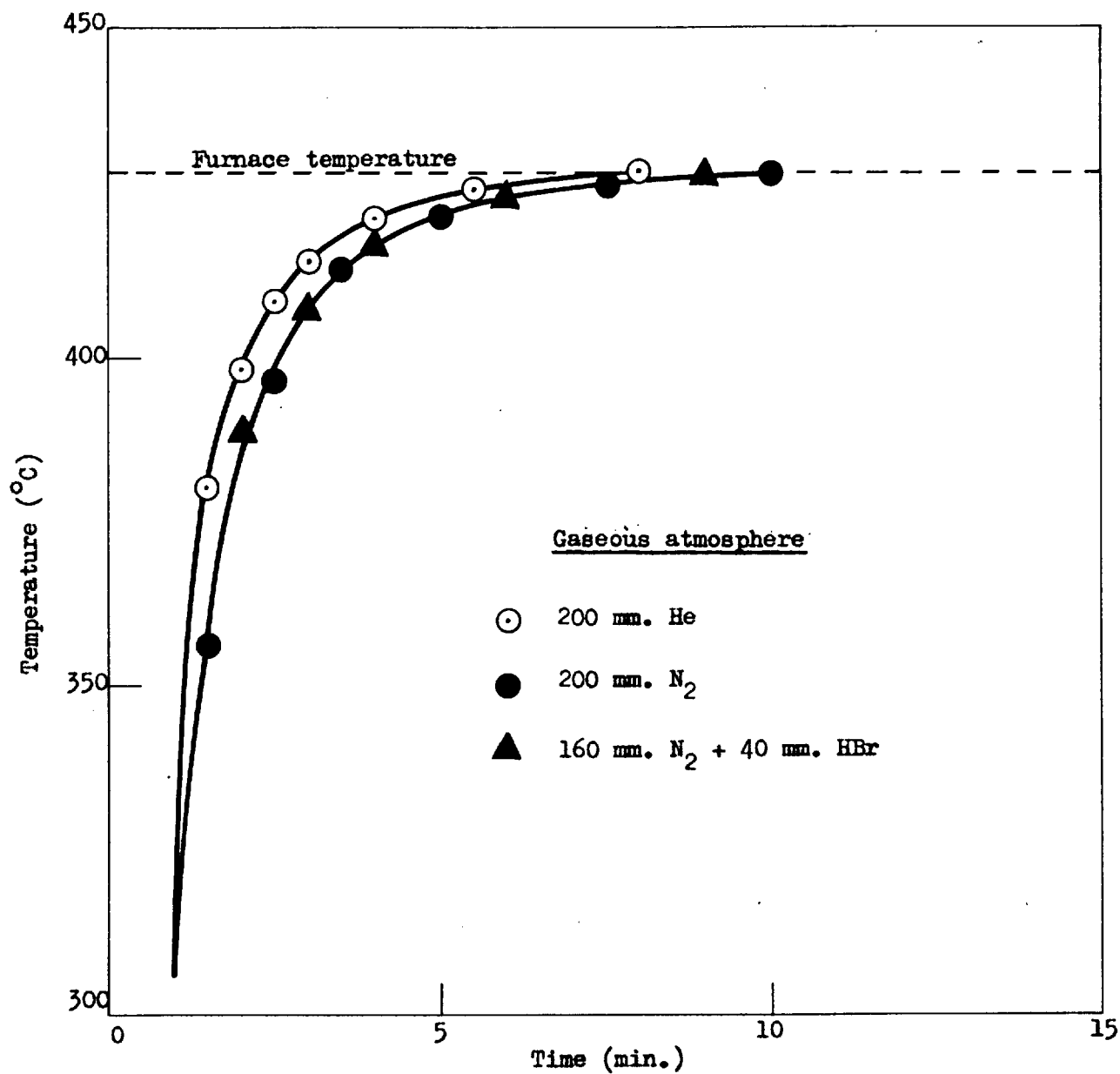


Figure 10

Influence of surrounding atmosphere on the rate of temperature rise of a thermocouple junction (system B)



hydrogen bromide mixture. The thermocouple junction attained the temperature of the reaction vessel after eight minutes in the helium atmosphere and after ten minutes in the nitrogen and nitrogen + hydrogen bromide atmospheres.

3. Influence of polymer sample on the rate of temperature rise

Measurements were made of the effect of a 300 mg. sample of polyethylene in the boat on the rate of temperature rise of the thermocouple junction arranged as in system B. In figure 11, this rate is compared with that obtained under otherwise identical conditions in the absence of the polymer. The rate of temperature increase and the final temperature were unaltered by the inclusion of the polymer sample but the temperature increase curve was displaced by about 30 seconds showing that the presence of the polymer increased the time taken for the thermocouple junction to attain the temperature of the furnace.

4. The time taken for the system to attain equilibrium

Figure 12(a) shows the pressure variation in the reaction vessel when the rod and boat are introduced at a given temperature into a nitrogen atmosphere. Equilibrium was attained after about six minutes. In all experiments where mention is made of the pressures of gases in the reaction vessel, these are given as the pressures appropriate to equilibrium conditions.

Figure 12(b) shows the variation of the temperature of the chromel-alumel thermocouple used in the furnace immediately after the introduction of the rod and boat into the reaction vessel. The time taken for the attainment of equilibrium conditions was between seven and eight minutes. In all experiments described subsequently, the

Figure 11

Influence of polymer sample on the rate of temperature rise of a thermocouple junction (system B)

Gaseous atmosphere: 200 mm. He

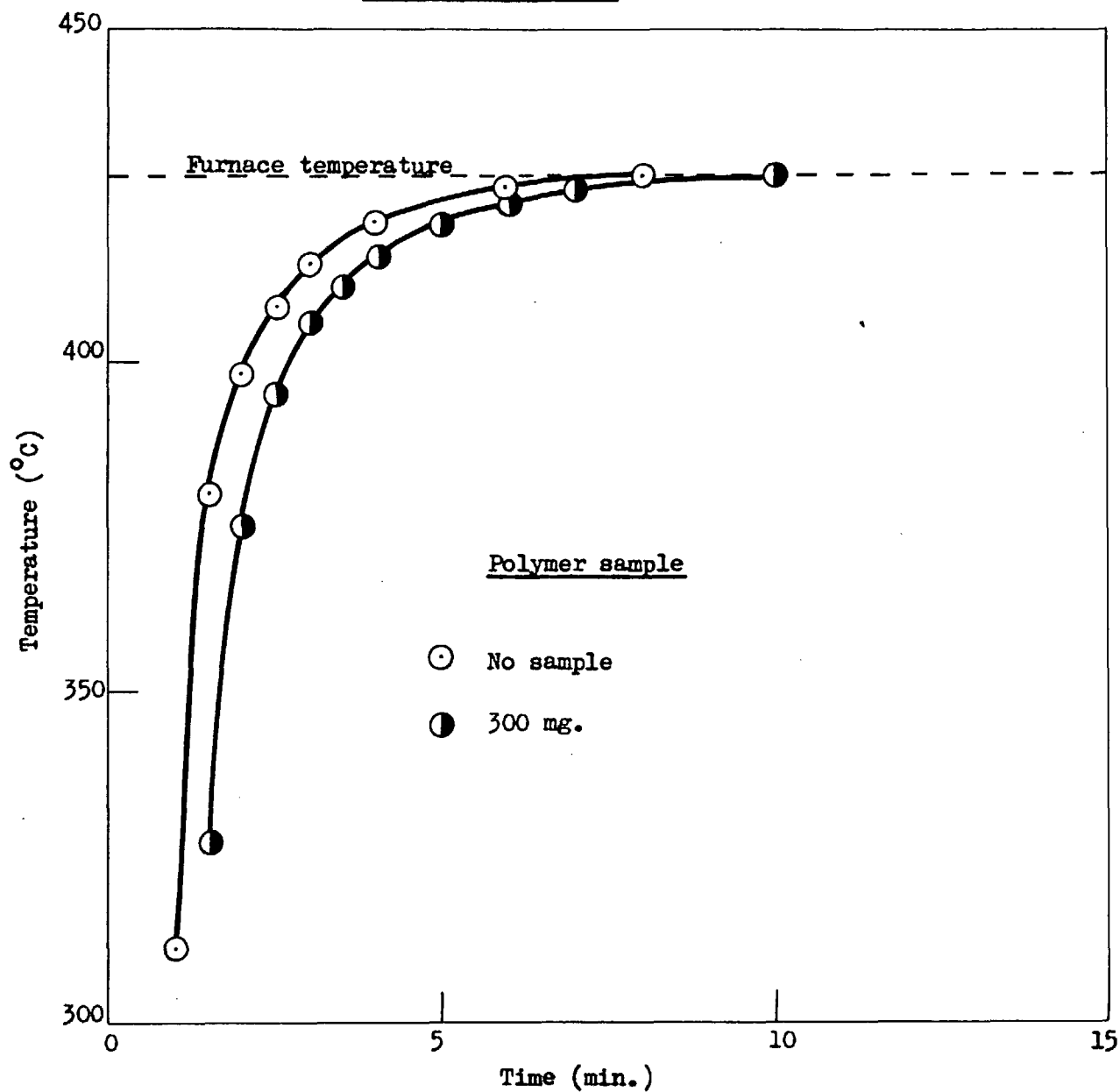
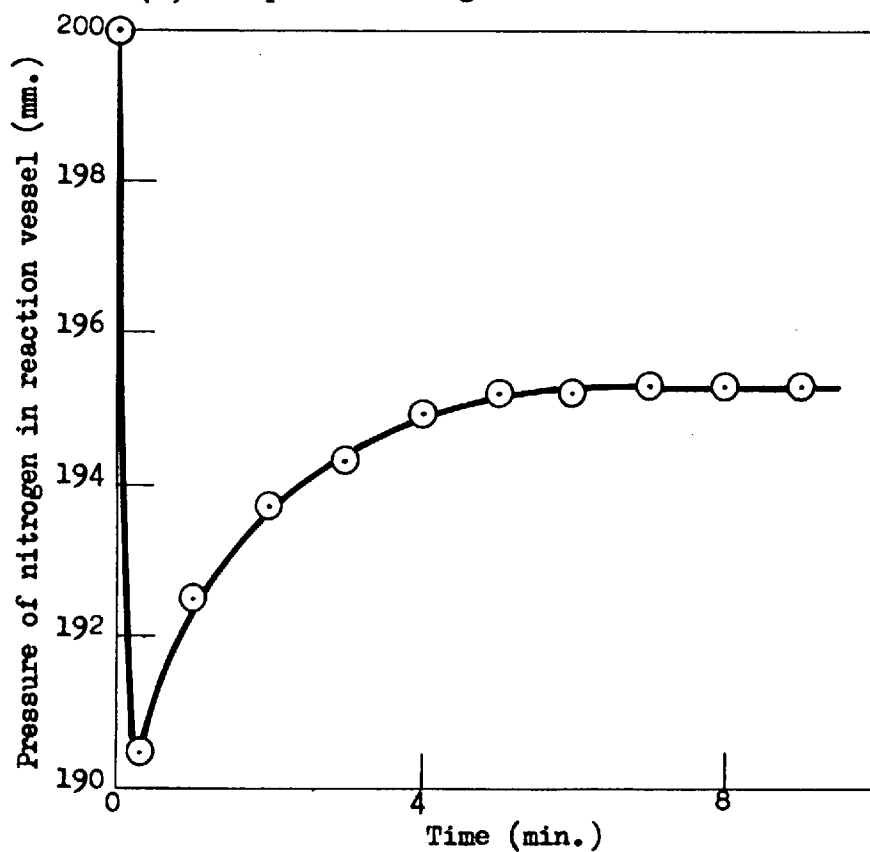


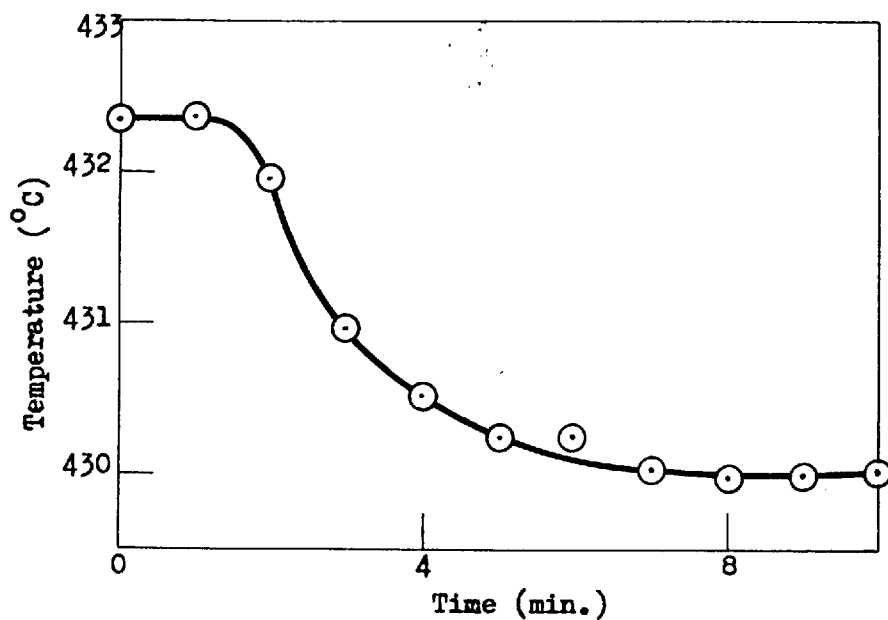
Figure 12

The variation, after introduction of the cold rod and boat into the reaction vessel, of:-

(a) the pressure of gas in the reaction vessel



(b) the temperature of the furnace thermocouple



temperature quoted is that which the system attained at equilibrium.

B The thermal degradation of polyethylene

1. Preliminary investigations

(a) Weight loss as a function of sample size

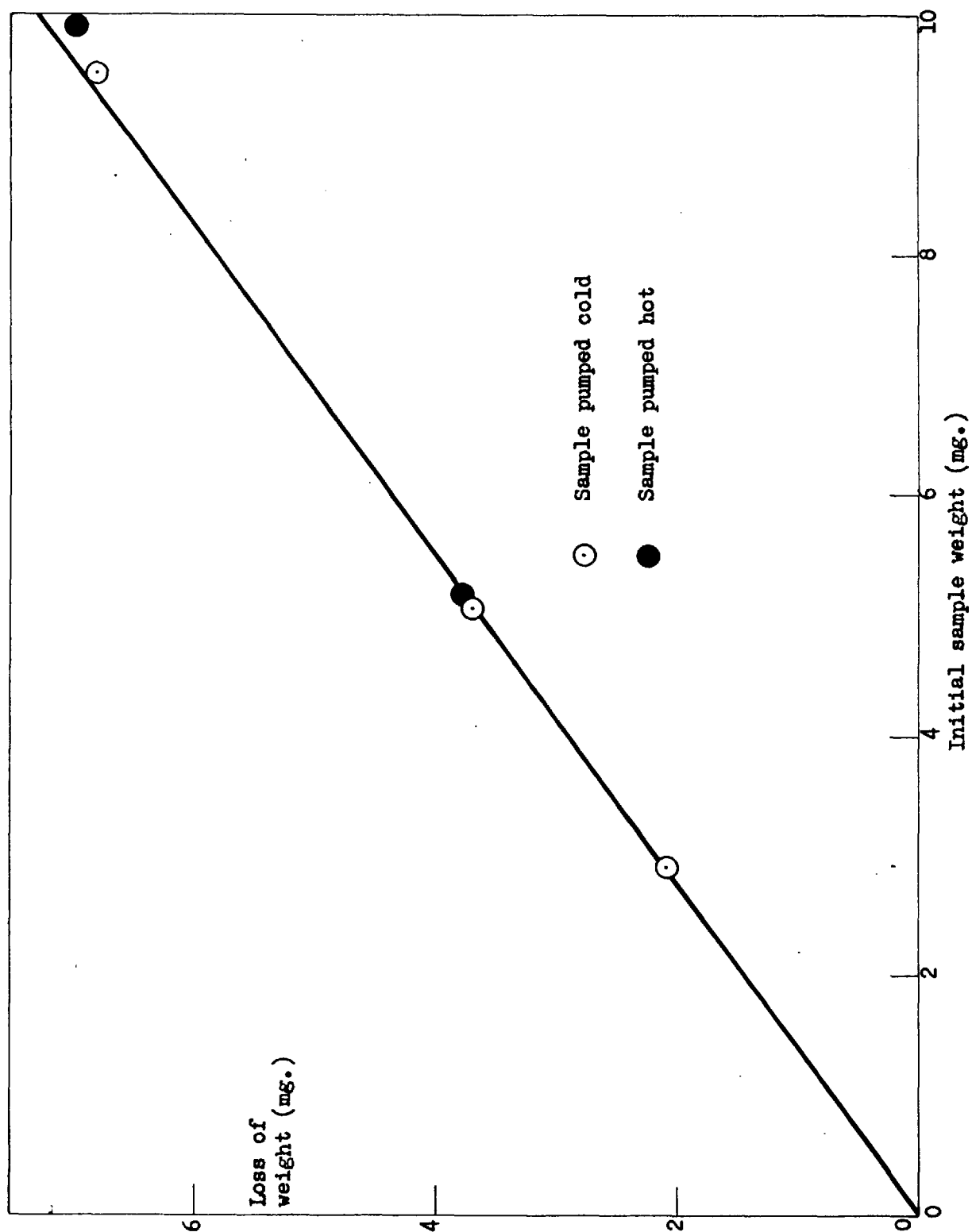
Samples of polyethylene of weights from 2.5 to 150 mg. were pyrolysed in nitrogen for 30 minutes and were then withdrawn from the reaction vessel. In some of these experiments the reaction vessel was pumped out after the sample had cooled and solidified whereas in other experiments the reaction vessel was pumped out immediately the sample was withdrawn. The results of these experiments are shown in figures 13 and 14.

The loss of weight of the polymer sample was unaffected by pumping out the reaction vessel while the sample was still hot. For small sample sizes, that is up to 10 mg. in size, there was a linear relationship between the sample size and the loss of weight after 30 minutes' pyrolysis. For larger sample sizes, however, the weight loss per mg. of sample was reduced (table 10).

(b) Thickness of the polymer sample

A number of observations were made on the thickness of the solidified polymer in the boat after withdrawal from the reaction vessel. This was done for varying sample weights, sufficient time being allowed for the sample first to melt. Below 20 mg. sample sizes the polymer tended to form discrete 'lumps' and for a 5 mg. sample it was estimated that the maximum depth of these was about 0.05 mm. With samples larger than about 20 mg. the solidified polymer formed a more

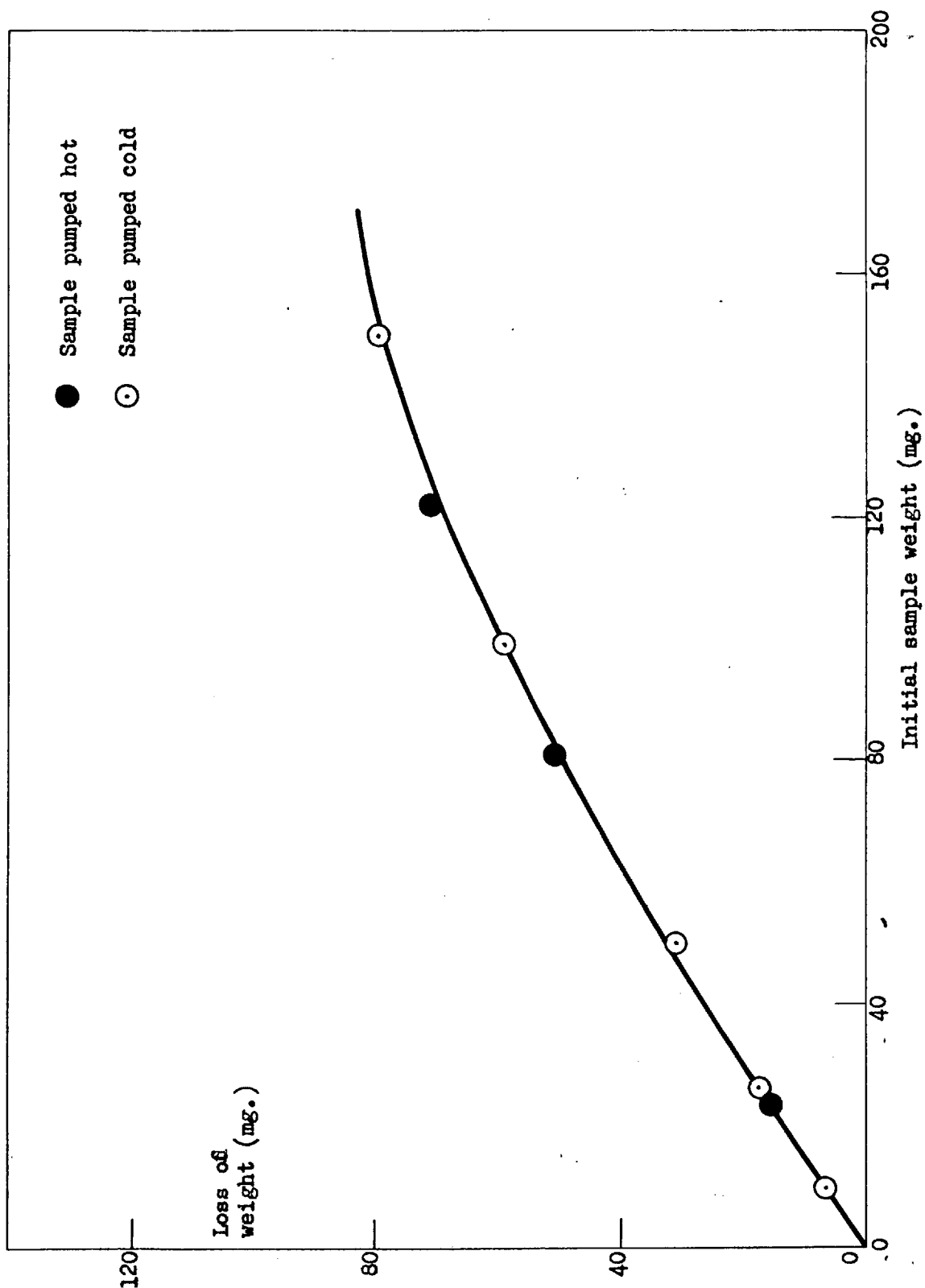
Figure 13



Loss of weight of polyethylene during pyrolysis: influence of initial sample weight

Temperature: 430°C Atmosphere: 200 mm. N₂ Pyrolysis time: 30 min.

Figure 14



Loss of weight of polyethylene during pyrolysis: influence of initial sample weight

Temperature: 430°C Atmosphere: 200 mm. N₂ Pyrolysis time: 30 min.

Table 10

Influence of sample size on the loss of weight of polyethylene samples during pyrolysis

Temperature: 430°C Gaseous atmosphere: 200 mm. nitrogen

$\frac{\Delta w}{w}$ = loss of weight (mg.) per mg. initial sample weight after
30 minutes' pyrolysis.

Weight of sample (mg.)	$\frac{\Delta w}{w}$
0-10	0.73*
20	0.63
50	0.61
100	0.59
150	0.52

* this value corresponds to the slope of the line in
figure 13.

even layer. The thickness of polymer samples of about 150 mg. weight was estimated to be of the order of 1 mm. It was noted that, as pyrolysis proceeded, the sample withdrawn had a waxy nature suggesting a large decrease in molecular weight; no discoloration or hardening was observed however.

(c) Influence of boat size on the loss of weight

Identical runs were performed using first the silica boat used throughout the work on pyrolysis and then a smaller silica boat used only for this comparison. Table 11 shows some of the results obtained for the pyrolysis of 5 mg. samples after various time intervals. The use of the smaller boat did not affect the rate of loss of weight of polyethylene during pyrolysis.

(d) Reproducibility in pyrolysis runs

Tests were made throughout the work on the reproducibility of the loss of weight measurements. To give some idea of the degree of reproducibility obtained, the results of a selection of repeated runs under various conditions are given in table 12. The loss of weight runs appeared to be reproducible to ± 0.05 mg.

(e) Influence of the form of sample

The polymer samples used in pyrolysis work were cut from the pellets of the polymer supplied by the Dow Chemical Co. Since in the work on oxidation the polymer was used in the form of a powder prepared from these pellets, some typical pyrolysis runs (in vacuum, nitrogen and hydrogen bromide) were repeated using the polymer in the powdered form. Loss of weight results, identical with those obtained from experiments using the polymer cut from the pellets, were recorded. This indicates **not** only that the form of the sample has little effect but also that the

Table 11

Influence of boat size on the loss of weight of polyethylene during pyrolysis

Sample weight: 5 mg.

Temperature: 430°C

Gaseous atmosphere: 200 mm. nitrogen

Time (min.)	Weight loss of polymer (mg.)	
	Large boat*	Small boat **
20	2.70	2.55
30	3.70	3.65
50	4.60	4.50

* Internal dimensions: 28 mm. long, 8 mm. wide, 9 mm. deep.

This boat was used throughout the rest of the work on pyrolysis and oxidation.

** Internal dimensions: 18 mm. long, 8 mm. wide, 7 mm. deep.

This boat was used only for this comparison.

Table 12

The reproducibility of loss of weight measurements during polyethylene pyrolysis

Gaseous atmosphere (partial pressure in mm.)	Pyrolysis time (min.)	Temperature (°C)	Loss of weight of 5 mg. sample in identical runs (mg.)	
			1	2
200 N ₂	45	430	4.45	4.35
190 N ₂ + 10 HBr	50	430	4.25	4.20
160 N ₂ + 40 HBr	180	400	2.40	2.40
160 N ₂ + 40 C ₂ H ₅ Br	45	430	3.95	3.90

stabiliser, which is present in the pellets but not in the powder (see p.74), has no appreciable influence on the reactions of the polymer at high temperatures.

2. Influence of the surrounding atmosphere on the rate of pyrolysis

(a) Pyrolysis in a vacuum

5 mg. samples of polyethylene were pyrolysed at 430°C in an evacuated reaction vessel. Two series of runs were performed. In the first, the reaction vessel was evacuated continuously while pyrolysis was in progress; in the second, the reaction vessel was isolated when the sample was introduced so that pyrolysis occurred in an atmosphere containing the volatile reaction products. The loss of weight of 5 mg. samples as a function of time is shown in figure 15. For each set of runs the plots of $\log_{10} w$ against t , where w mg is the weight of the residue after t minutes, were linear (figure 16); thus the rate of loss of weight is in both cases first-order with respect to residue weight. The first-order rate constants are given in table 13. Continuous evacuation of the reaction vessel during pyrolysis appears to increase the rate of loss of weight of the polymer with respect to pyrolysis in an isolated system.

(b) Pyrolysis in nitrogen

The loss of weight of a 5 mg. sample pyrolysed at 430°C is plotted as a function of time in figure 15. The first-order plot for this reaction was linear and the corresponding rate constant is given in table 13. A comparison of the relevant rate constants in table 13 shows that the presence of an inert gas decreases the rate of loss of weight of the polymer with respect to the rate of loss of weight in a vacuum.

Figure 15

Pyrolysis of polyethylene in a vacuum and in nitrogen

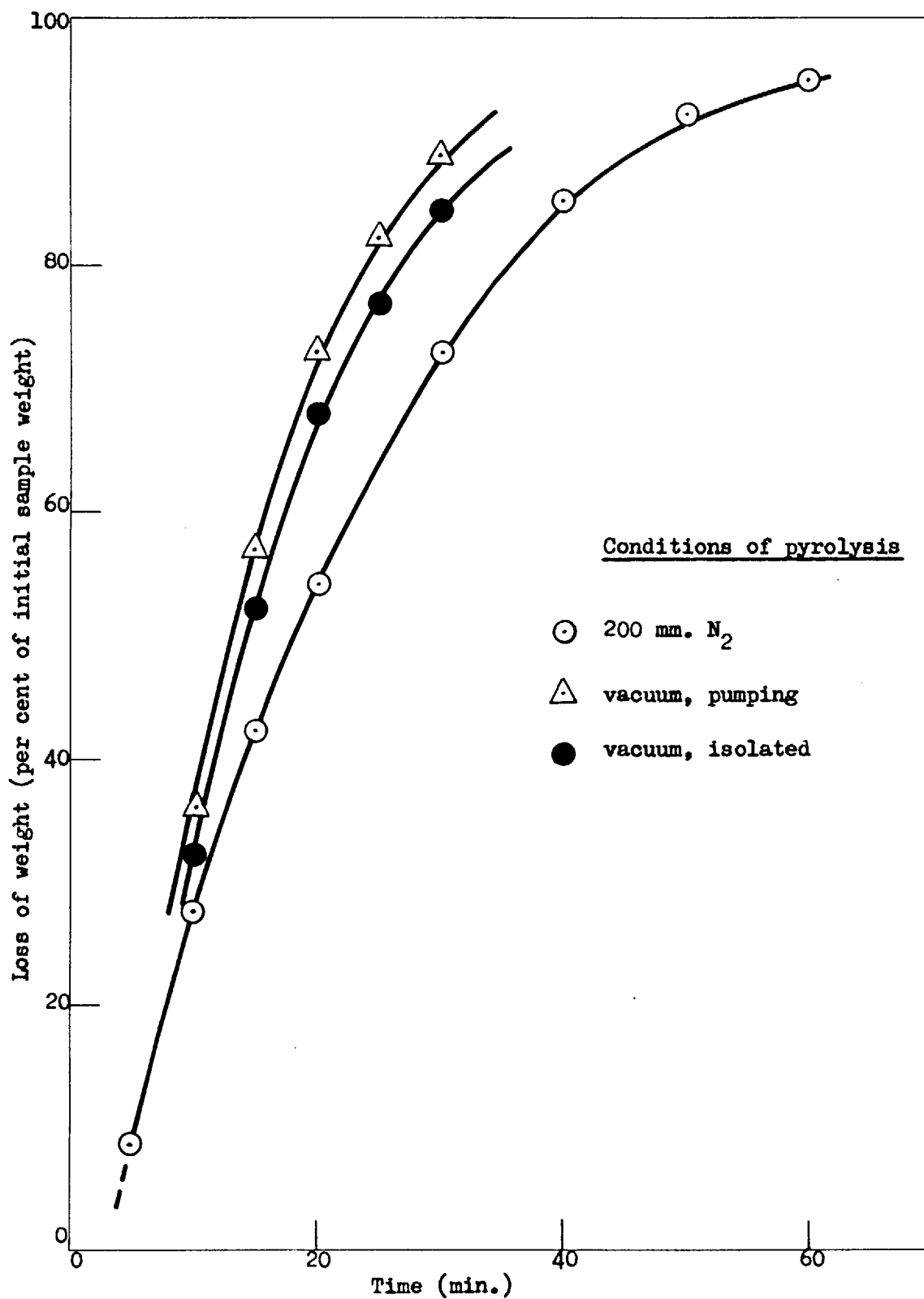
Temperature: 430°CSample weight: 5 mg.

Figure 16

First-order plot of loss of weight results from pyrolysis of polyethylene in a vacuum

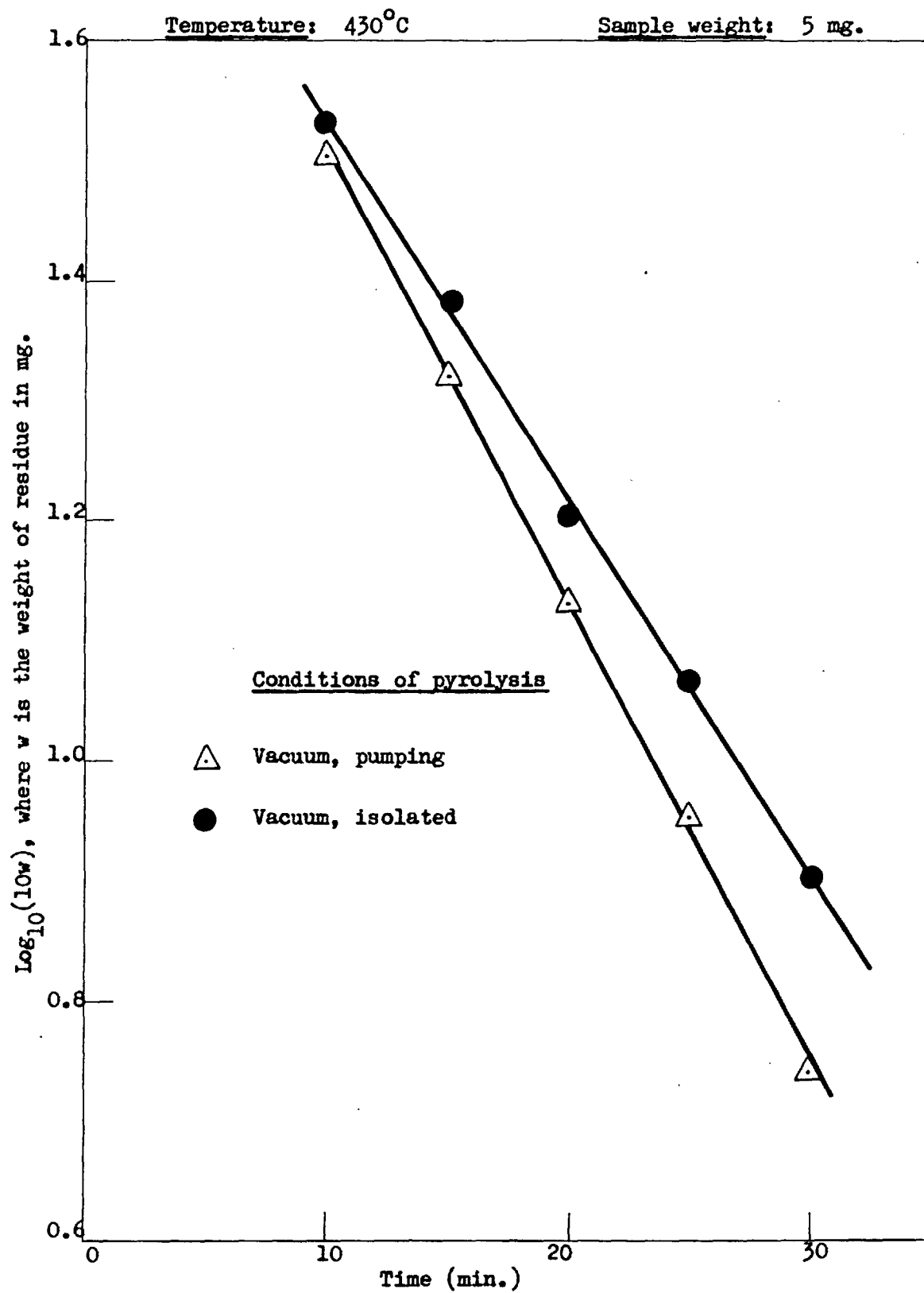


Table 13

Influence of surrounding atmosphere on first-order rate constants
for the rate of loss of weight of polyethylene

Temperature: 430°C

Gaseous atmosphere	Rate constant $k \times 10^2$	
	(min ⁻¹)	(sec ⁻¹)
Vacuum (pumping)	8.71	0.145
Vacuum (isolated)	7.37	0.123
200 mm. nitrogen	5.48	0.0913
200 mm. helium	5.47	0.0912

(c) Influence of nitrogen pressure

The loss of weight of polymer samples during pyrolysis in the presence of different nitrogen pressures is shown in figure 17. The effect on the rate of pyrolysis of nitrogen pressure appeared to be negligible in the pressure range 100-400 mm.

(d) Influence of the nature of the inert gas

(i) Helium compared with nitrogen

Figure 18 shows the loss of weight as a function of time during pyrolysis in helium compared with the loss of weight in nitrogen under otherwise identical conditions. For a given time of pyrolysis, more of the polymer had volatilised in helium than in nitrogen. Linear first-order plots are shown in figure 19 and the rate constants obtained from them are given in table 13. It appears that the rate of pyrolysis in helium is the same as that in nitrogen. A more thorough investigation of the kinetics of these reactions was made as follows.

The rates of loss of weight ($-dw/dt$ mg. min⁻¹) for given residue weights (w mg.) were obtained by drawing tangents to the curves in figure 18. In figure 20 the values of $\log_{10} (-dw/dt)$ were plotted against w for pyrolysis in both helium and nitrogen. Three slopes were obtained from the points in this figure; these are defined and their values are given in table 14. The slope of the best straight line in this figure is unity and the other slopes also approximate to unity. This agrees with the deduction from figure 19 that in both cases the rate of loss of weight of the polymer during pyrolysis is proportional to the weight of the residue left.

Figure 17

Influence of the pressure of nitrogen on the pyrolysis of polyethylene

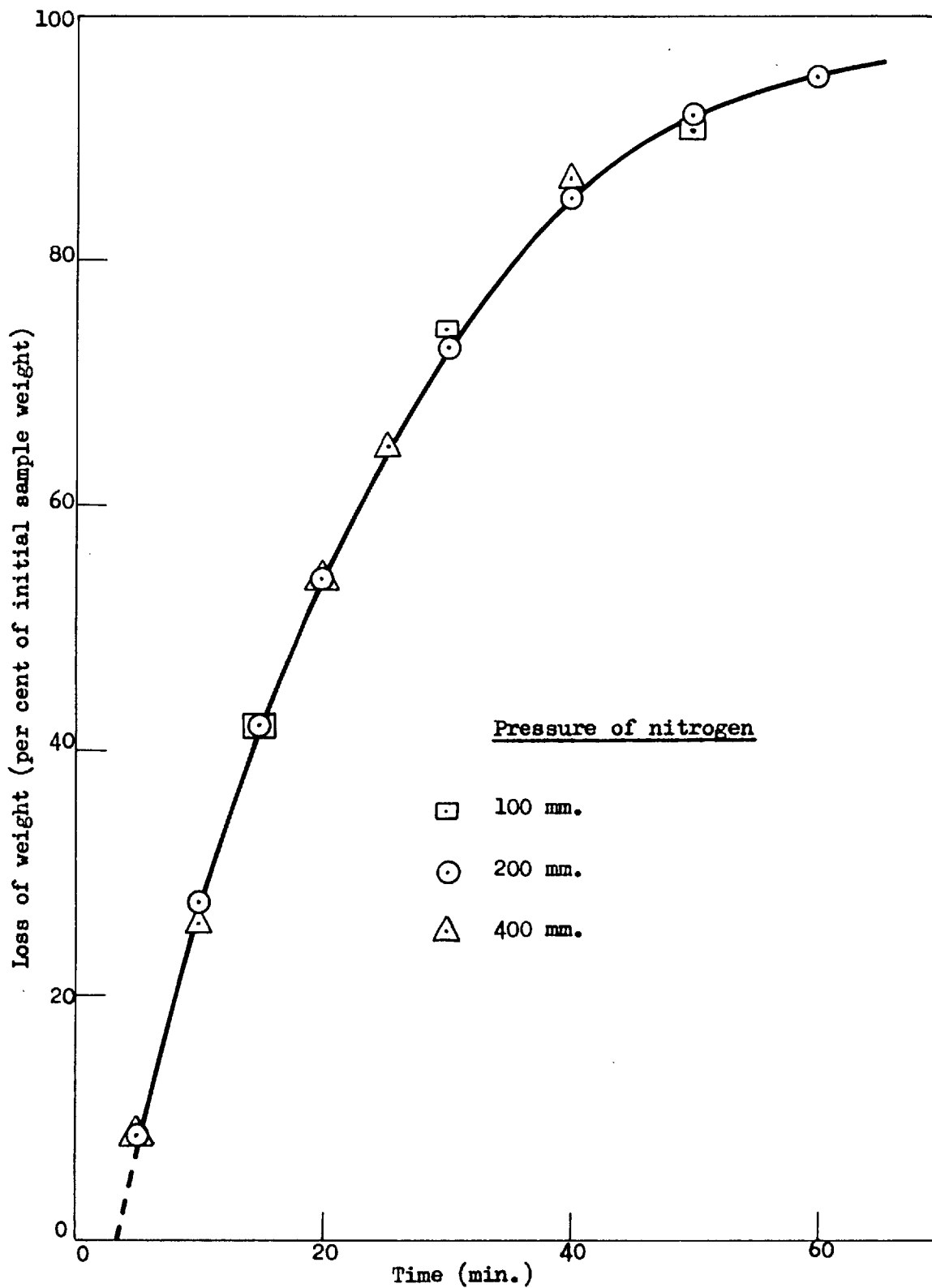
Temperature: 430°CSample weight: 5 mg.

Figure 18

Influence of inert gas on the pyrolysis of polyethylene

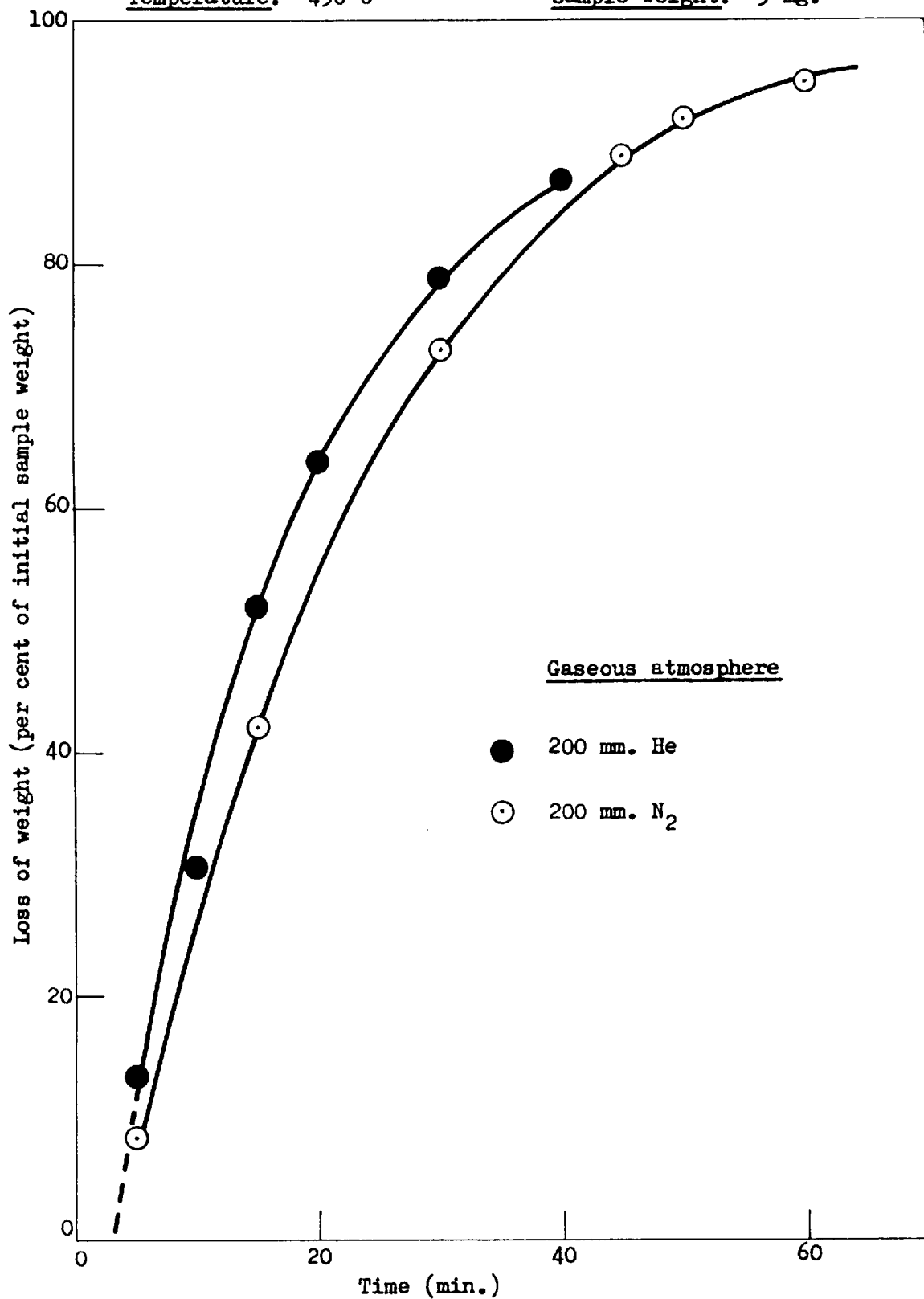
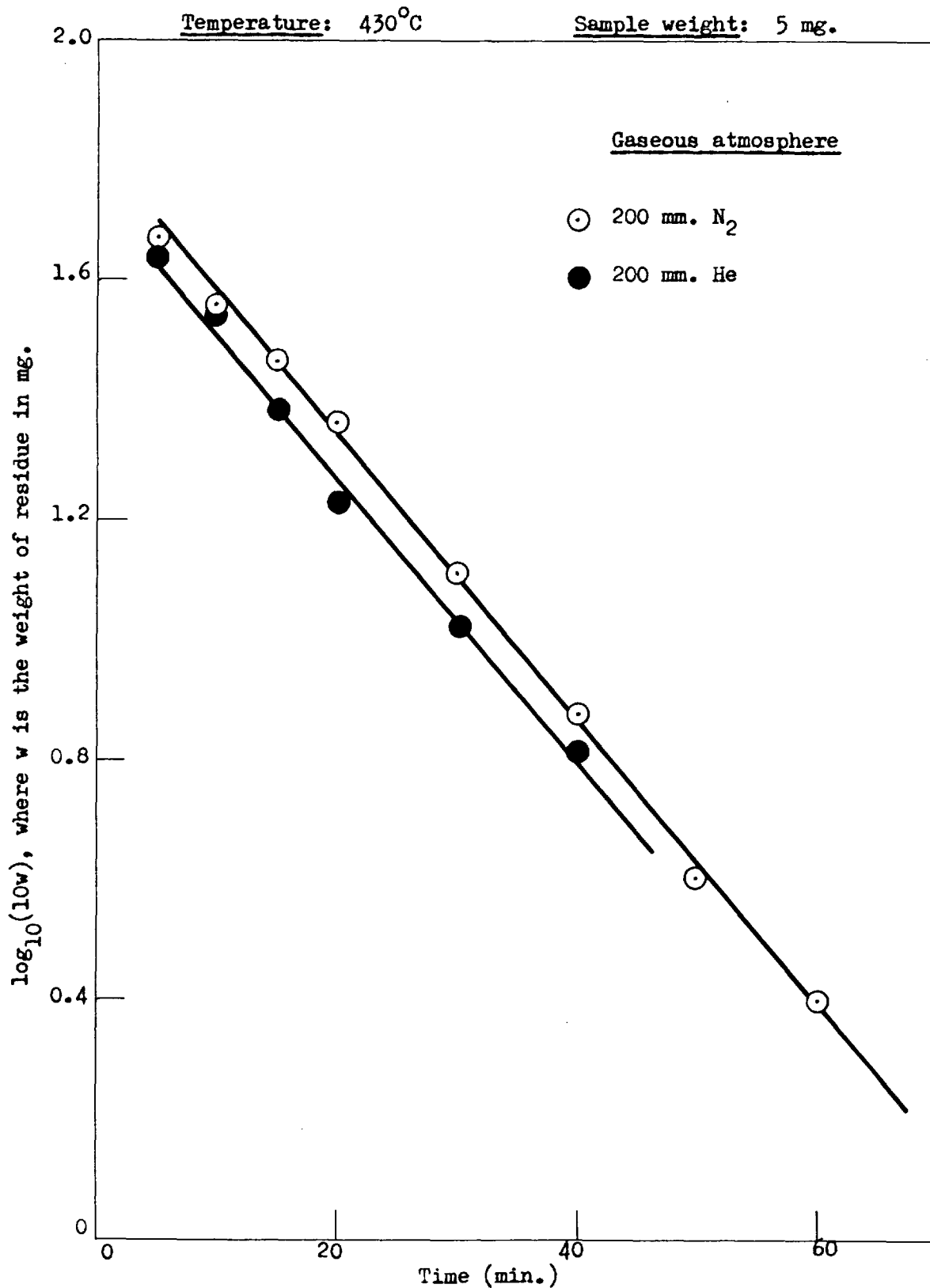
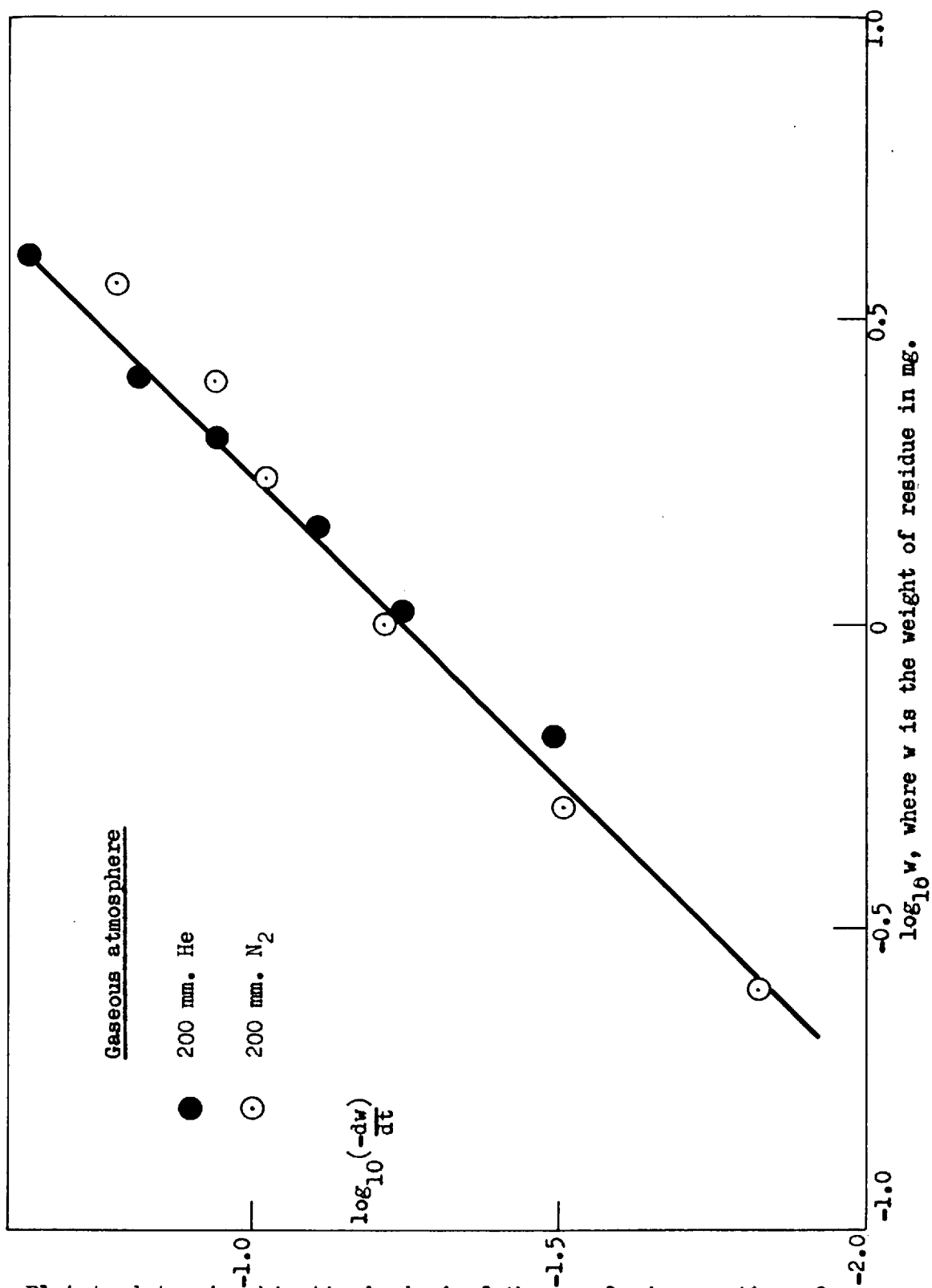
Temperature: 430°CSample weight: 5 mg.

Figure 19
First-order plots of loss of weight results from pyrolysis of
polyethylene in inert gas atmospheres





Plot to determine kinetic 'order' of the pyrolysis reaction of polyethylene in inert gas atmospheres

Temperature: 430°C

Sample weight: 5 mg.

Table 14

The kinetic 'order' of the pyrolysis of polyethylene in inert gas atmospheres

Temperature: 430°C

Best straight line in fig.20 drawn as described below	Slope and hence 'order'
Through all the points	1.0
Through points corresponding to helium	1.1
Through points corresponding to nitrogen	0.9

In figure 21, $-dw/dt$ is plotted as a function of w for pyrolysis in helium and nitrogen. In helium, a linear relationship was obtained throughout the whole course of the reaction investigated whereas in nitrogen this was only the case in the later stages of the pyrolysis. In the initial stages of the reaction (up to about 20 minutes' pyrolysis) the rate of loss of weight was less than that in helium. In the derivation of the rate constant for pyrolysis in nitrogen from the results shown in figure 18 the points representing the initial stages of pyrolysis were ignored.

From this analysis of the results it may be concluded that the rate of loss of weight of polyethylene during pyrolysis in helium and during the later stages of the pyrolysis in nitrogen is represented by an equation of the form

$$-dw/dt = kw$$

where k , the rate constant, is the same for pyrolysis in both helium and nitrogen.

(ii) Hydrocarbon gases

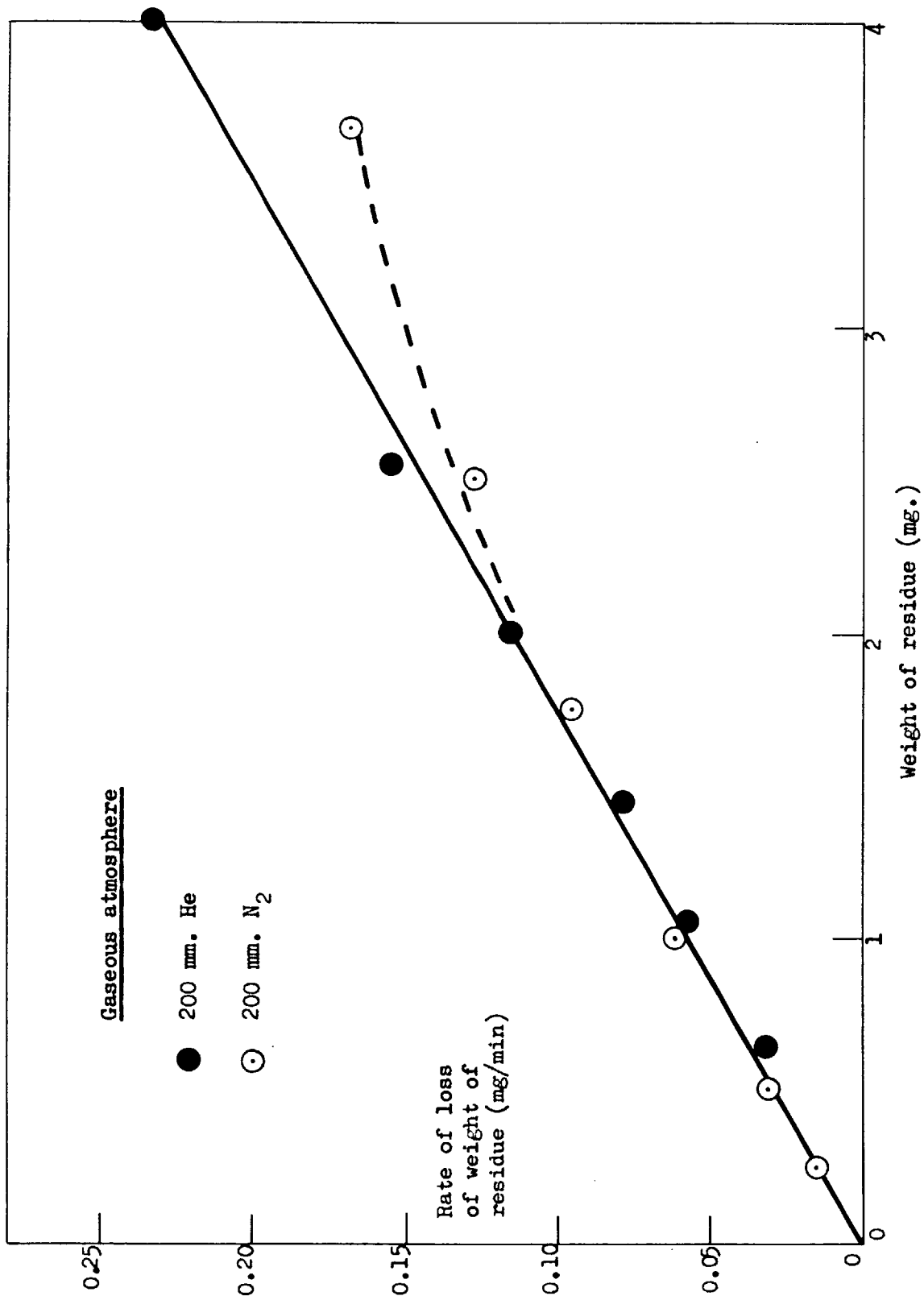
The rate of loss of weight of polyethylene in nitrogen was found to be virtually unaffected by the addition of hydrocarbon gases. Table 15 shows loss of weight measurements obtained in atmospheres containing propene, pentane and pent-1-ene compared with those obtained in a pure nitrogen atmosphere.

3. Influence of hydrogen bromide

(a) Influence of hydrogen bromide on the rate of pyrolysis

The loss of weight of polyethylene samples undergoing

Figure 21



Influence of inert gas on the rate of loss of weight of polyethylene during pyrolysis

Temperature: 430°C

Sample weight: 5 mg.

Table 15

Influence of hydrocarbon gases on the pyrolysis of polyethylene

Temperature: 430°C

Sample weight: 5 mg.

Time of pyrolysis (min.)	Gaseous atmosphere (partial pressure in mm.)			
	200 nitrogen	40 propene + 160 nitrogen	40 pentane + 160 nitrogen	40 pent-1-ene + 160 nitrogen
	Loss of weight (per cent)			
30	73	72	74	73
45	89	-	87	87
60	95	-	93	96

degradation in a nitrogen + hydrogen bromide mixture was investigated at 430 and 400°C. The results obtained are compared in figures 22 and 23 with those obtained for pyrolysis in nitrogen under otherwise identical conditions. In each case, for a given time of pyrolysis the loss of weight during pyrolysis in the hydrogen bromide atmosphere was less than that observed during pyrolysis in nitrogen.

Values of the rate of loss of weight for given residue weights were calculated from the loss of weight curves and are plotted as a function of residue weight in figures 24 and 25. At 430°C, for pyrolysis in both nitrogen and a nitrogen + hydrogen bromide mixture a strictly linear relationship was obtained only during the later stages of pyrolysis (figure 24). At this temperature, in both atmospheres, the rate of loss of weight per mg. of polymer residue was less in the initial stages of the reaction than that observed in the later stages of the reaction. At 400°C an approximately linear relationship between the rate of loss of weight and the residue weight was observed throughout the range investigated for pyrolysis in both nitrogen and the nitrogen + hydrogen bromide mixture.

The loss of weight results (figures 22 and 23) were used to obtain the first-order plots shown in figures 26 and 27; the corresponding rate constants are given in table 16. From these data, the activation energies of the pyrolysis reactions of the polymer, in the presence and absence of hydrogen bromide, were obtained (table 16).

From these results it is clear that the presence of hydrogen bromide substantially reduces the rate of loss of weight of polyethylene during pyrolysis. The effect of hydrogen bromide on the overall

Figure 22

Loss of weight of polyethylene during pyrolysis showing the influence of hydrogen bromide

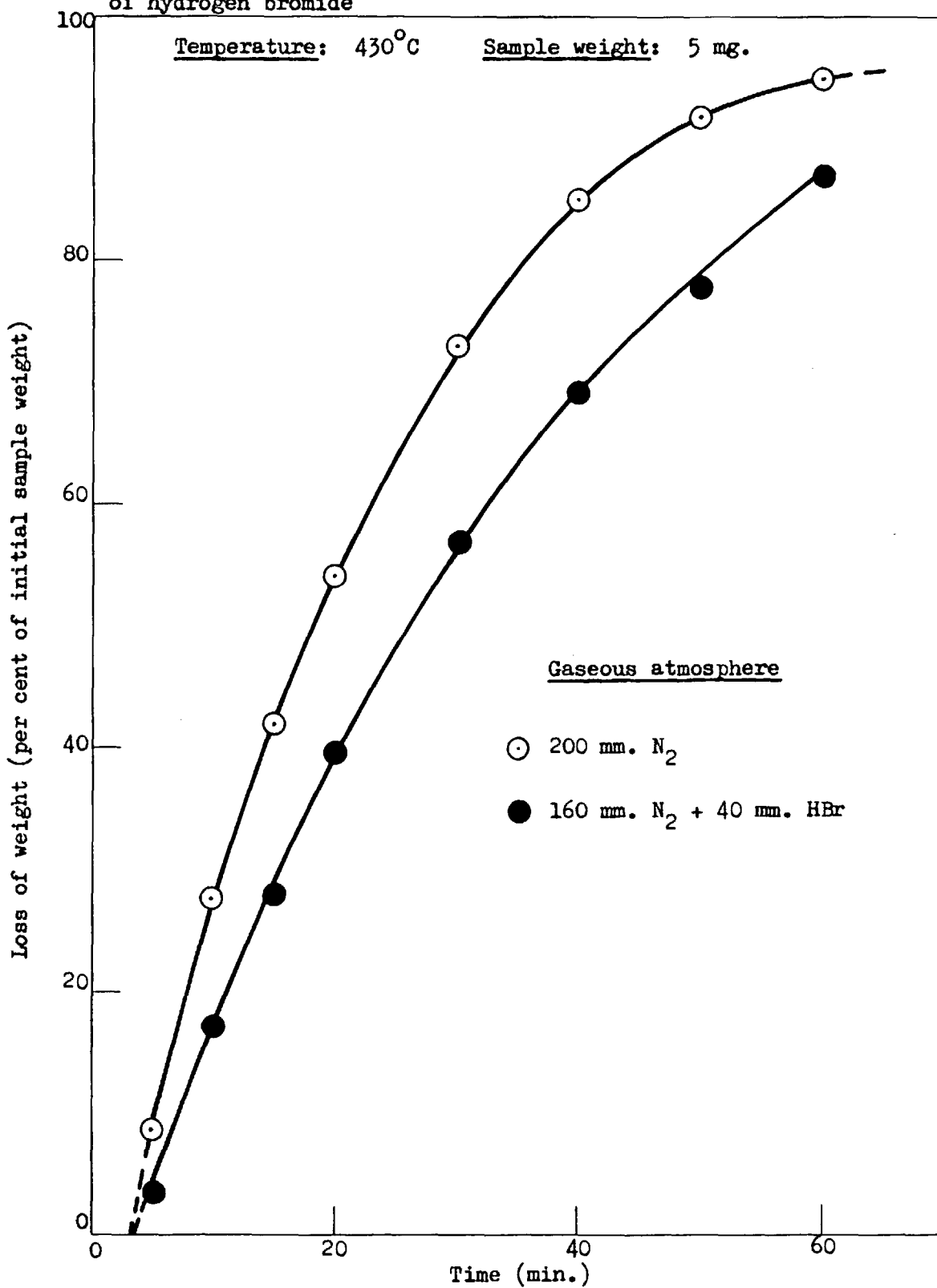
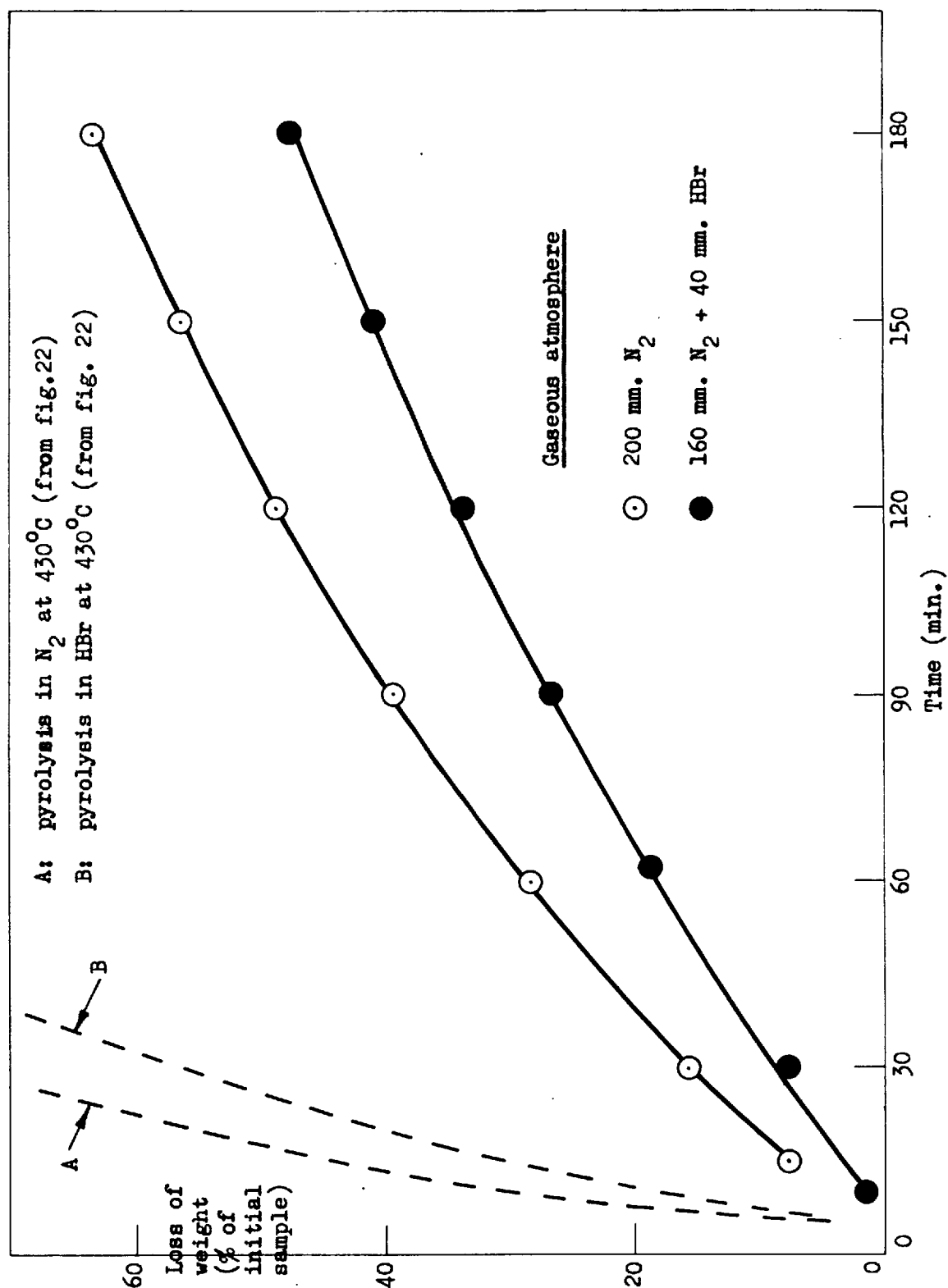


Figure 23

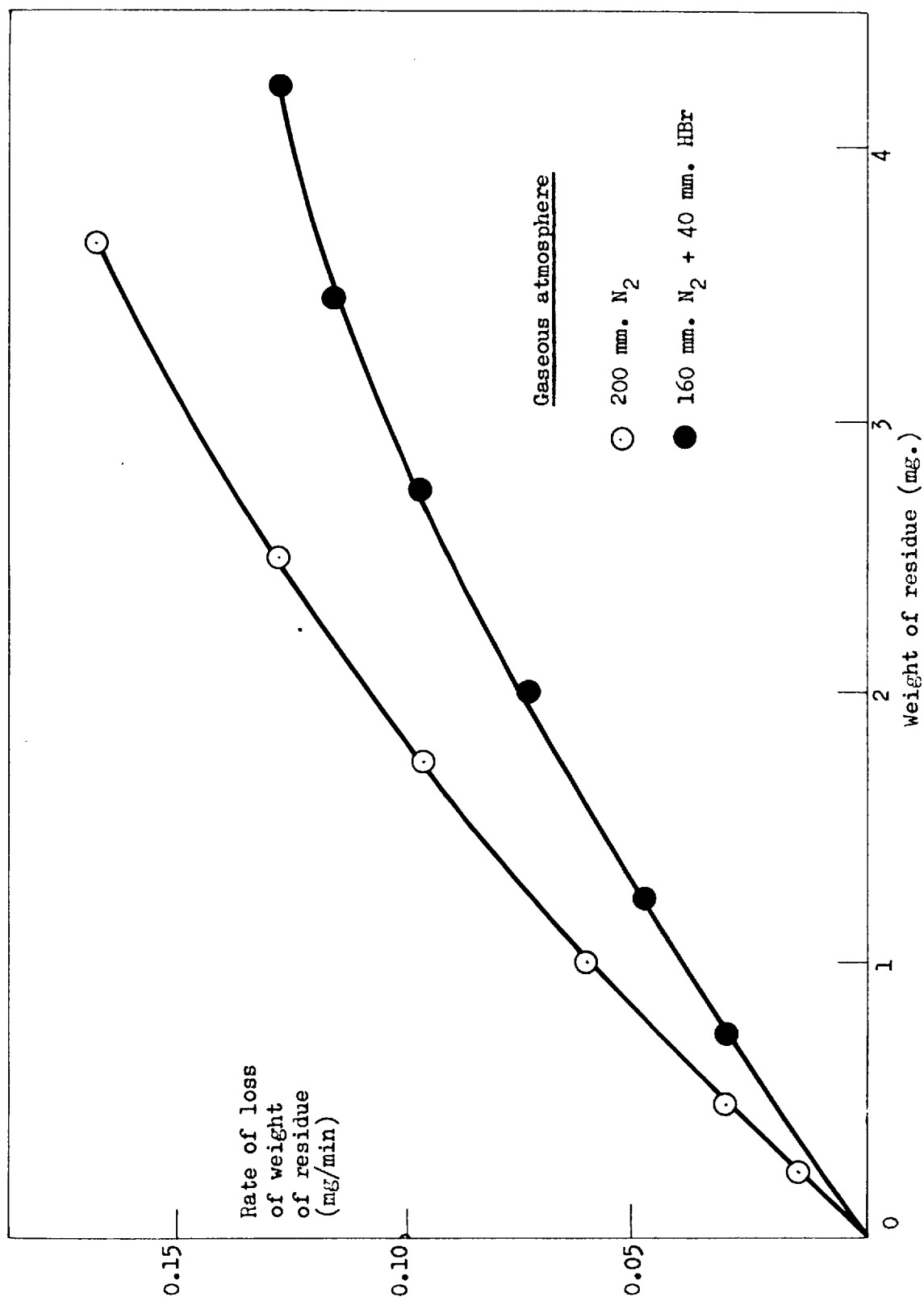


Loss of weight of polyethylene during pyrolysis showing influence of hydrogen bromide

Temperature: $400^\circ C$

Sample weight: 5 mg.

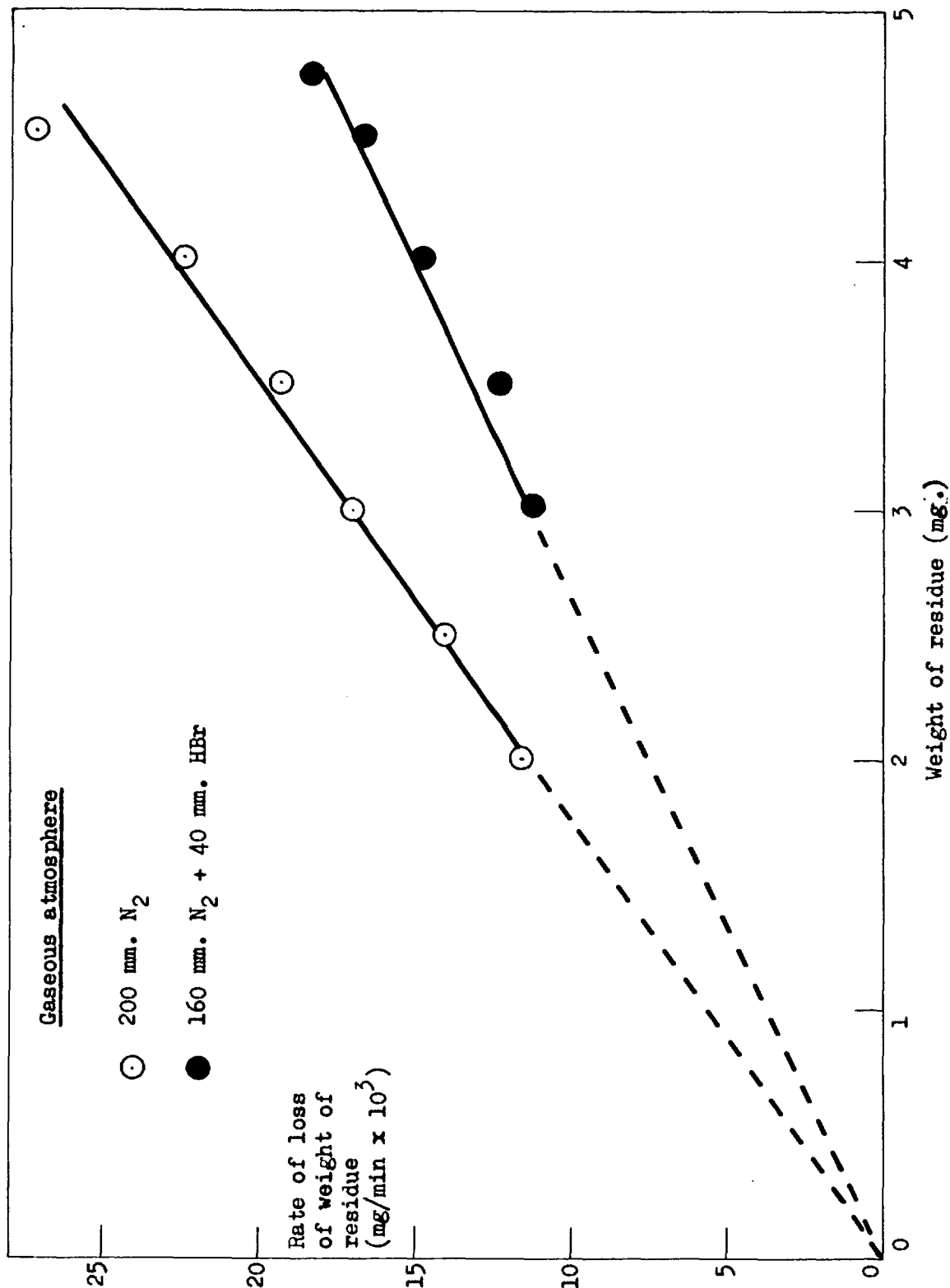
Figure 24



Influence of hydrogen bromide on the rate of loss of weight of polyethylene during pyrolysis

Temperature: 430°C

Sample weight: 5 mg.



Influence of hydrogen bromide on the rate of loss of weight of polyethylene during pyrolysis

Temperature: 400°C

Sample weight: 5 mg.

Figure 26

First-order plots of loss of weight results from the pyrolysis of polyethylene showing the influence of hydrogen bromide

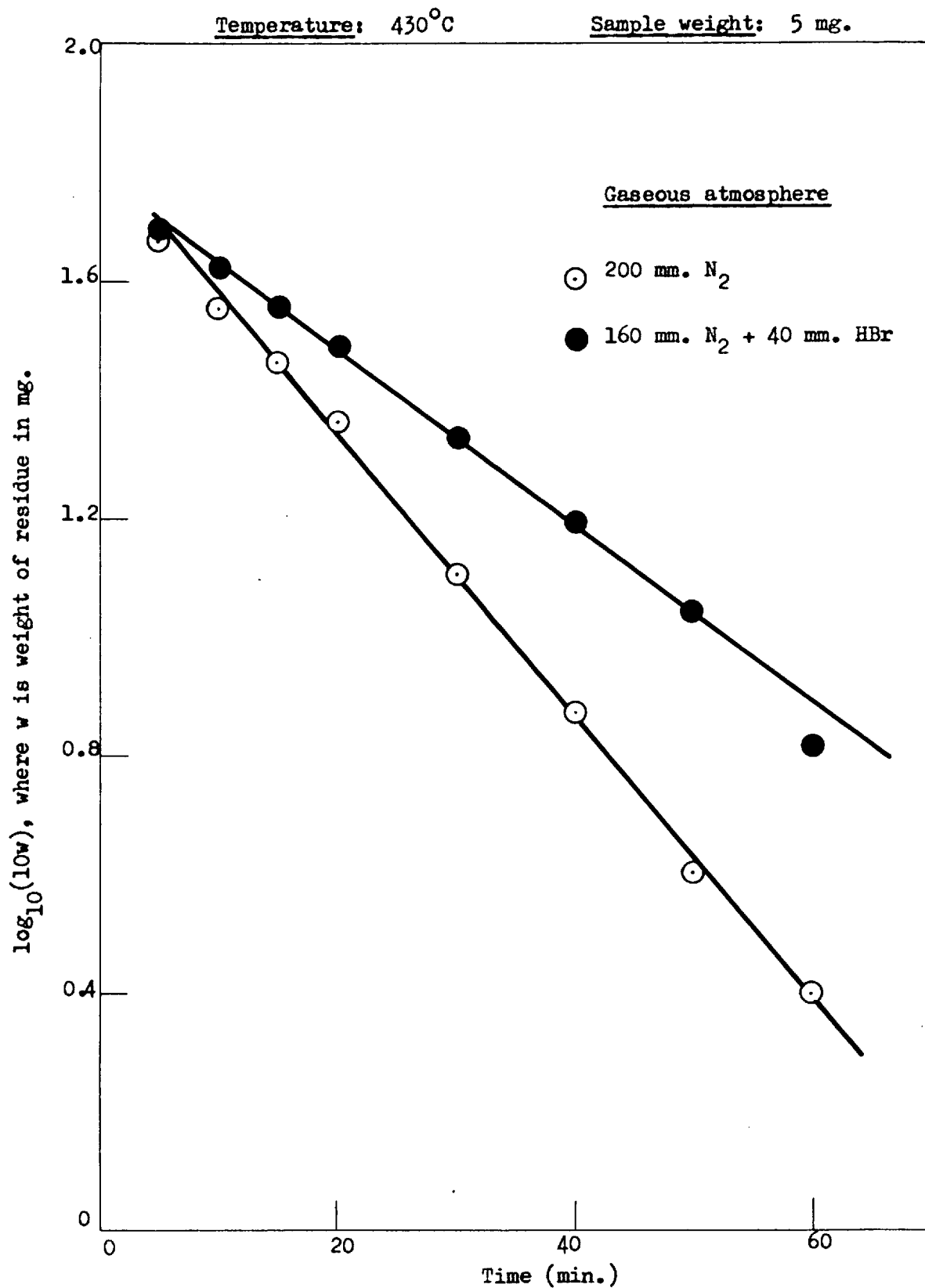
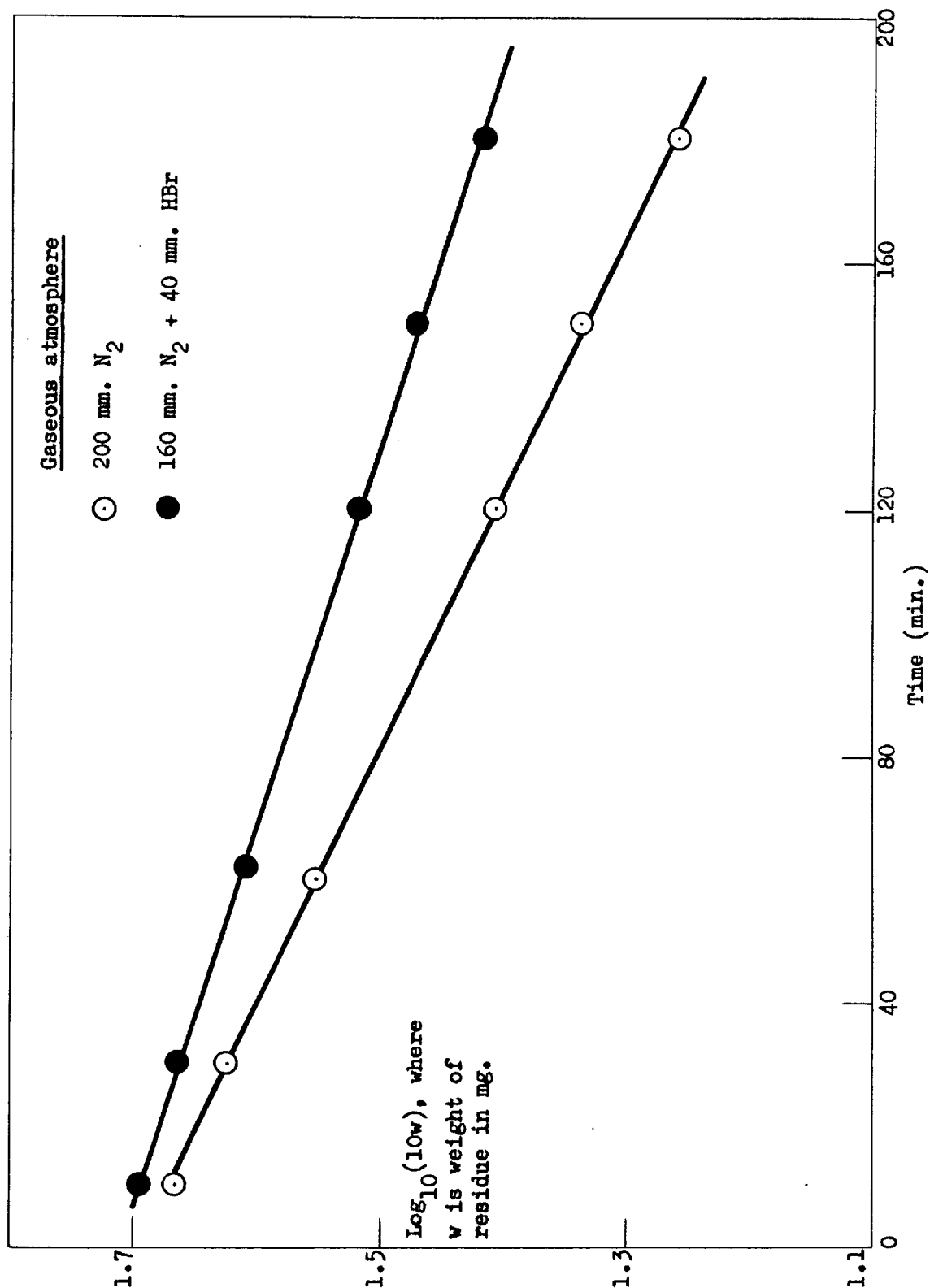


Figure 27



First-order plots of loss of weight results from the pyrolysis of polyethylene showing the influence of hydrogen bromide

Temperature: 400°C

Sample weight: 5 mg.

Table 16

Rate constants and activation energies for the pyrolysis of polyethylene showing the influence of hydrogen bromide

Gaseous atmosphere	Temperature (°C)	Rate constant (min ⁻¹)	Overall activation energy (kcal/mole)
200 mm. N ₂	430	5.48×10^{-2}	72
	400	5.60×10^{-3}	
160 mm. N ₂ + 40 mm. HBr	430	3.40×10^{-2}	69
	400	3.74×10^{-3}	

activation energy of the degradation of polyethylene appears, however, to be small.

(b) Influence of hydrogen bromide concentration

The effect of varying the pressure of hydrogen bromide present during pyrolysis, while maintaining the total pressure constant, was investigated by loss of weight measurements on 5 mg. samples of polymer after 30 and 50 minutes' pyrolysis. Some of the results are shown in figure 28. The extent of volatilisation after a given time decreased approximately linearly with the concentration of hydrogen bromide. It was unfortunately not possible to make any quantitative deductions as to the effect of the concentration of the additive on the rate of pyrolysis since the differences in the readings in this series of measurements were comparable with the experimental error.

(c) Influence of total pressure

The influence on the extent of pyrolysis of the partial pressure of nitrogen in the presence of a constant quantity of hydrogen bromide was investigated by loss of weight measurements. Some of the results obtained are shown in table 17. The influence of nitrogen, in the range investigated, appeared to be small.

(d) Analysis of the residue after pyrolysis in hydrogen bromide

Analysis was carried out on residues obtained by pyrolysis of 20 mg. samples of polyethylene in an atmosphere containing hydrogen bromide. The results of the analytical measurements are shown in table 18. No bromine was found in the polymer residues and the carbon: hydrogen ratio was found in all cases to be approximately 1:2.

Figure 28

Influence of the partial pressure of hydrogen bromide on the extent of pyrolysis of polyethylene

Temperature: 430°C

Sample weight: 5 mg.

Total pressure (with N₂): 200 mm.

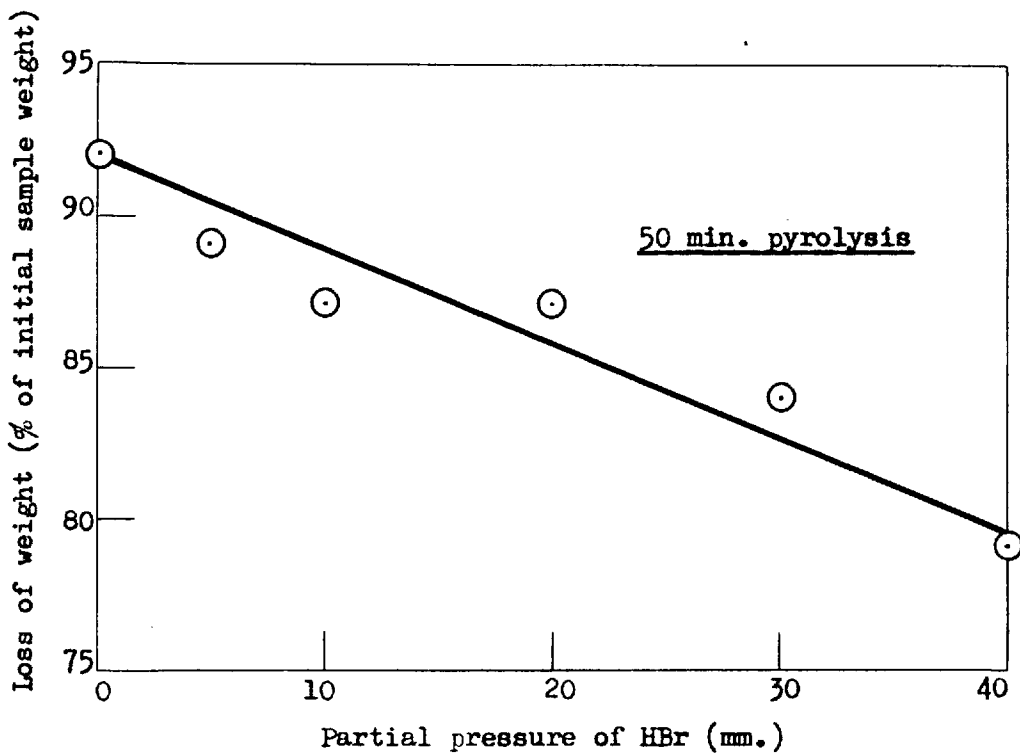
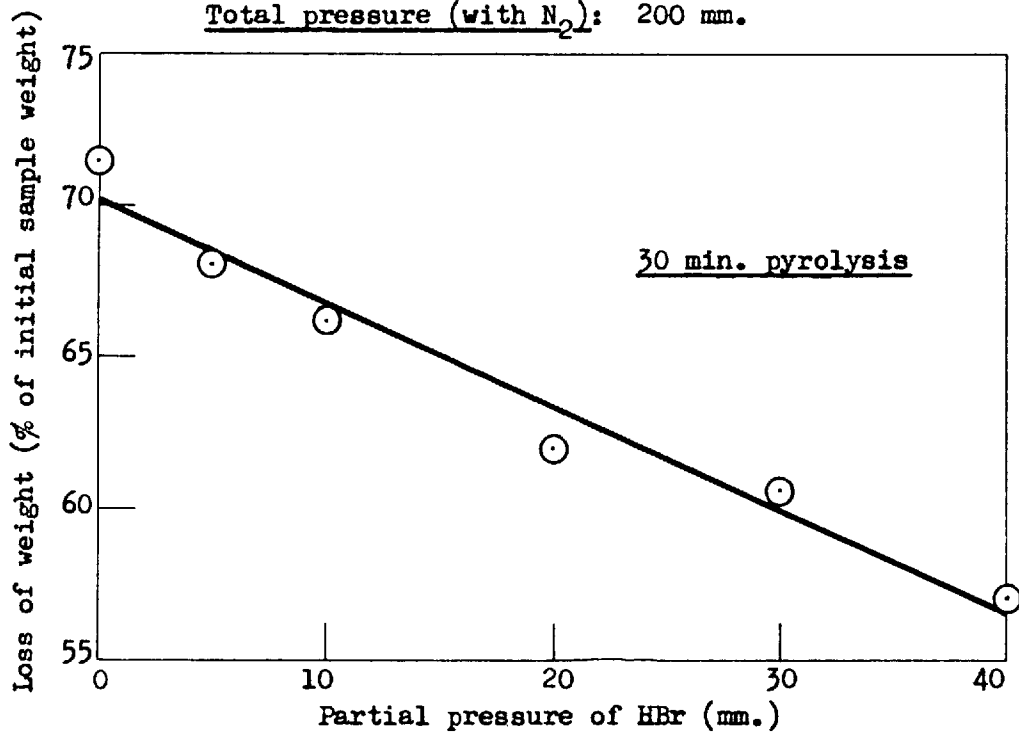


Table 17

Influence of total pressure on the extent of pyrolysis of polyethylene in hydrogen bromide

Temperature: 430°C

Sample weight: 5 mg.

Partial pressure of hydrogen bromide : 40 mm.

Added gas : nitrogen

Time of pyrolysis : 50 minutes

Total pressure N ₂ + HBr (mm.)	Loss of weight (per cent)
100	79
200	78
300	78
400	80

Table 18

Analysis of residue obtained by pyrolysis of polyethylene
showing the influence of hydrogen bromide

Temperature : 430°C

Sample weight : 20 mg.

Gaseous atmosphere (partial pressure in mm.)	Time of pyrolysis (min.)	Per cent by weight in residue		H : C
		Carbon	Hydrogen	
200 N ₂	30	85.6	14.7	2.0
160 N ₂ + 40 HBr	15	85.7	14.4	2.0
160 N ₂ + 40 HBr	30	86.0	13.5	1.9
160 N ₂ + 40 HBr	50	85.9	14.1	2.0

4. Influence of organic bromine compounds on the rate of
pyrolysis

(a) Additives with one bromine atom per molecule

The loss of weight of 5 mg. samples of polyethylene at 430°C was investigated during pyrolysis in the presence of bromomethane, bromoethane, 1-bromopropane and 2-bromopropane. In each case the atmosphere used contained 160 mm. of nitrogen and 40 mm. of bromine compound and the appropriate gas mixture was introduced into the reaction vessel at the same time as the polymer sample. The loss of weight curves obtained are shown in figure 29.

It was observed, on comparison of figure 29 with figure 22, that with bromomethane as an additive the loss of weight curve followed, almost exactly, that obtained for pyrolysis in pure nitrogen under similar conditions. On the other hand, the curves obtained for pyrolysis in 1-bromopropane and 2-bromopropane approximated to that obtained for pyrolysis in an equivalent quantity of hydrogen bromide. The curve obtained for pyrolysis in bromoethane was intermediate between these two extremes.

Linear first-order plots for pyrolysis in bromomethane, 1-bromopropane and 2-bromopropane were obtained and the rate constants derived from them are given in table 19 together with those obtained for the pyrolysis in nitrogen and hydrogen bromide. The effect of bromomethane on the rate of loss of weight appears to be slight whereas the effect of 1-bromopropane and 2-bromopropane is marked. Both of these additives decreased the rate of pyrolysis with respect to the rate in pure nitrogen to a value approximating to that observed for pyrolysis in

Figure 29

Loss of weight of polyethylene during pyrolysis in the presence of organic bromides

Temperature: 430°C

Sample weight: 5 mg.

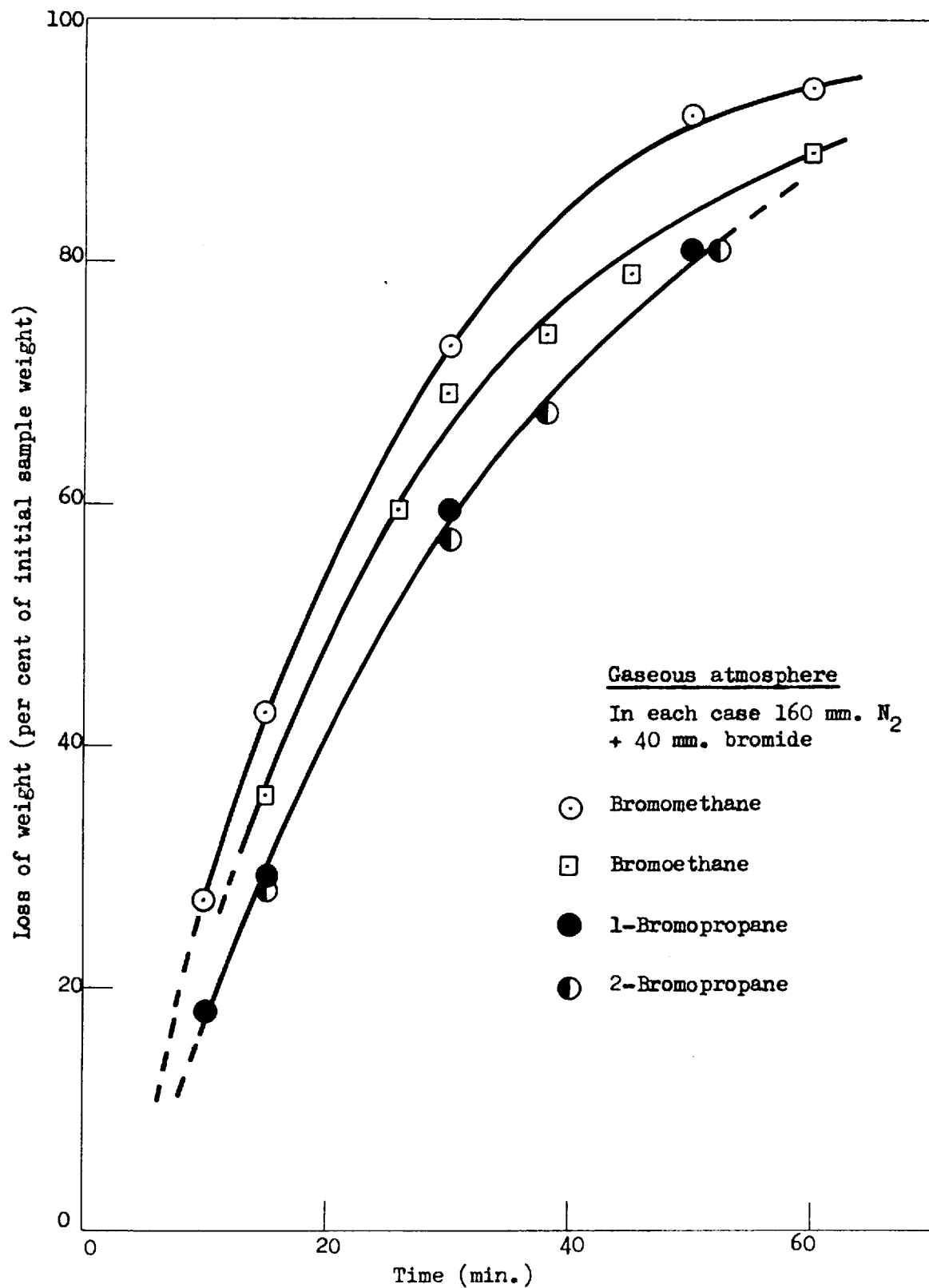


Table 19

Influence of organic bromides on rate constants for the loss of weight of polyethylene during pyrolysis

Gaseous atmosphere (partial pressure in mm.)	First-order rate constant $\times 10^2$ (min^{-1})
200 nitrogen	5.48
40 hydrogen bromide + 160 nitrogen	3.40
40 bromomethane + 160 nitrogen	5.18
40 bromoethane + 160 nitrogen	4.83 *
	3.86 **
40 1-bromopropane + 160 nitrogen	3.90
40 2-bromopropane + 160 nitrogen	3.58

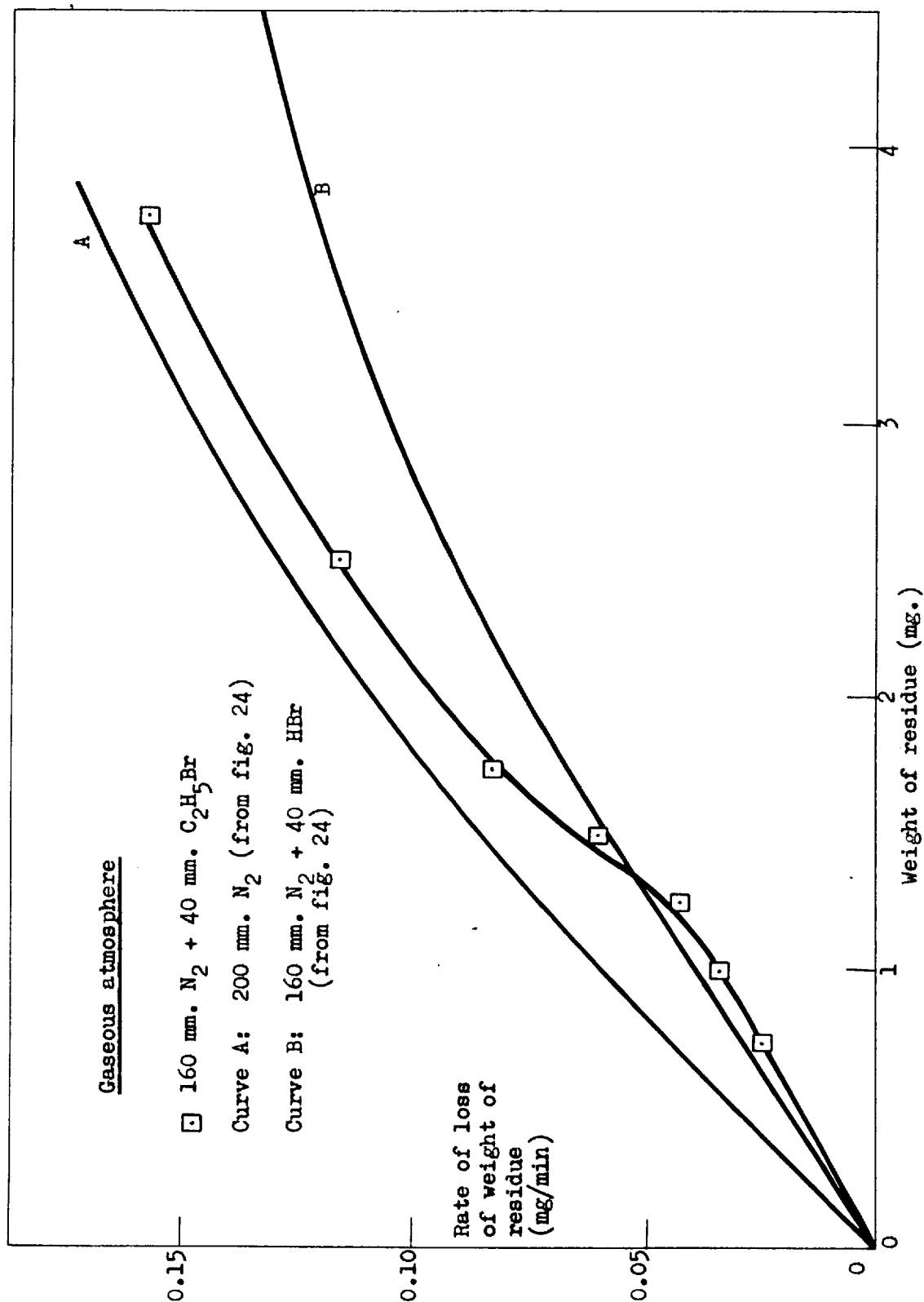
* mean value for 15-70% weight loss

** mean value for 70-90% weight loss

an atmosphere containing an equivalent quantity of hydrogen bromide. The rate of pyrolysis in 1-bromopropane was slightly greater than that in 2-bromopropane.

A first-order plot of the results obtained for pyrolysis in bromoethane proved to be non-linear. First order rate constants were obtained, however, for the initial stages and the later stages of the reaction and these are given in table 19. The values obtained suggest that the rate of loss of weight decreased as pyrolysis proceeded in the presence of this additive. An analysis of the kinetics of the degradation reaction in the presence of bromoethane was also made in the following manner. Values of $-dw/dt$ (mg. min.^{-1}) for given residue weights, w mg., were obtained from the loss of weight curve. A plot of $-dw/dt$ against w is shown in figure 30 in which the corresponding curves for pyrolysis in pure nitrogen and an equivalent quantity of hydrogen bromide are also given. In the initial stages of the pyrolysis in bromoethane the rate of loss of weight approximated to that observed in pure nitrogen but, as pyrolysis continued, the rate decreased to that observed in the hydrogen bromide atmosphere.

The influence of bromomethane and bromoethane was also investigated using initial sample sizes of 150 mg. The results obtained are compared with those obtained, under otherwise identical conditions, in nitrogen and in a nitrogen + hydrogen bromide mixture in figure 31. The curves obtained from experiments in which the additives were introduced into the reaction vessel at the same time as the polymer sample (as was the case in all the experiments using 5 mg.



Influence of bromoethane on the rate of loss of weight of polyethylene during pyrolysis

Temperature: 430°C

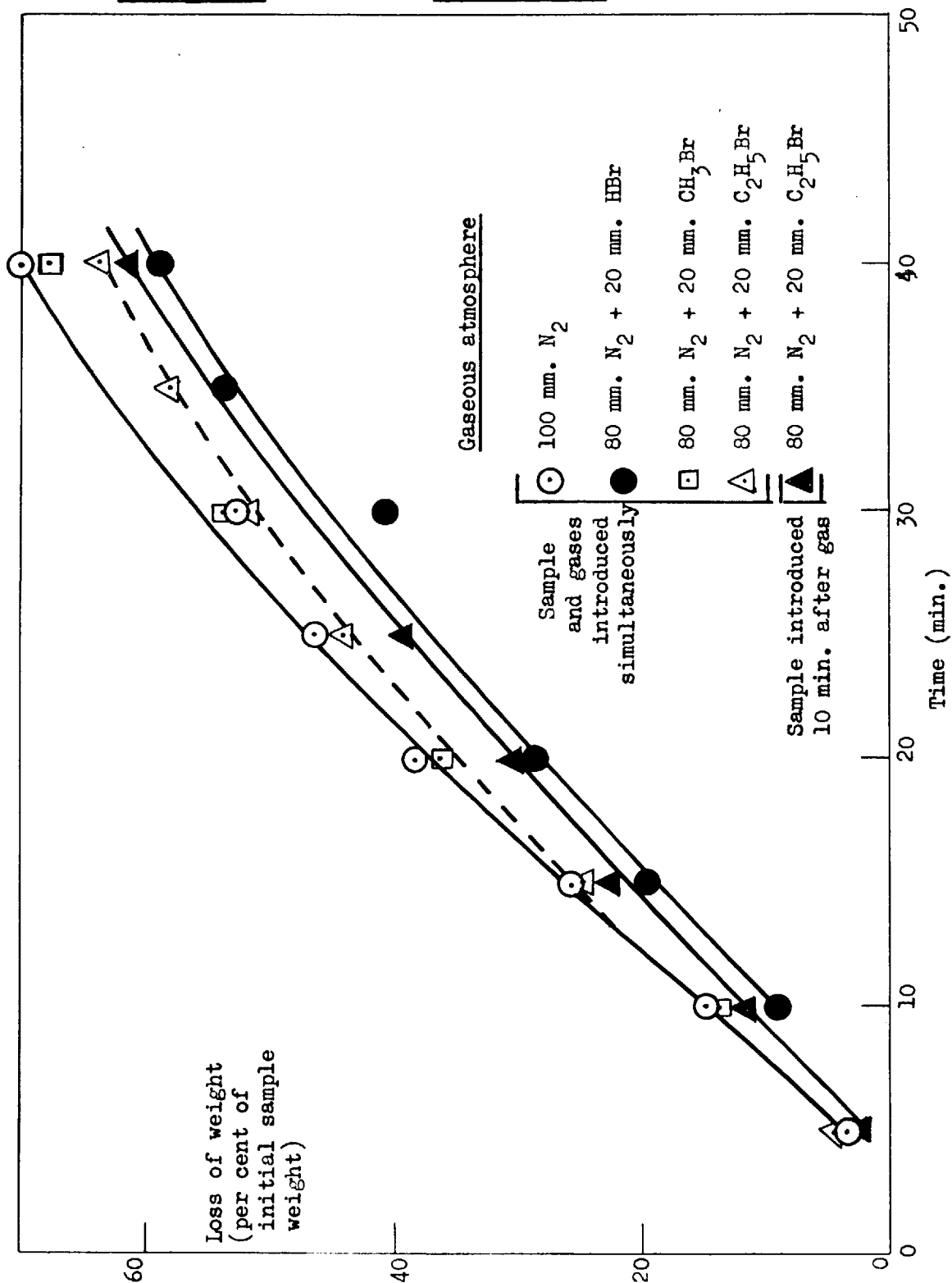
Sample weight: 5 mg.

Figure 31

Loss of weight of polyethylene during pyrolysis showing the influence of volatile bromine compounds

Temperature: 430°C

Sample weight: 150 mg.



samples described previously) show that the effects are similar to those found with 5 mg. samples of polymer. Thus with bromomethane as the additive the rate of loss of weight was almost identical with that observed in its absence; with bromoethane as the additive the rate of loss of weight, although initially uninfluenced, decreases as pyrolysis proceeds. Figure 31 shows, however, one effect which was not investigated with 5 mg. samples. When the atmosphere containing bromoethane was introduced into the reaction vessel ten minutes before the polymer sample, the rate of loss of weight was decreased at once to approximately the same value as that found in the presence of an equivalent quantity of hydrogen bromide.

(b) Additive with two bromine atoms per molecule

Pyrolysis was followed using an atmosphere containing 10 mm. of 1,2-dibromoethane and 190 mm. of nitrogen. The vapour pressure of this additive is such that attempts to increase its partial pressure would have caused it to condense in the cold outer tube. The results of the three loss of weight measurements made are shown in figure 32. The curves for pyrolysis in nitrogen and a nitrogen + hydrogen bromide mixture are shown for comparison. It appears that 1,2-dibromoethane reduces the extent of loss of weight after a given pyrolysis time with respect to pyrolysis in pure nitrogen. The effect is somewhat less than that produced by 10 mm. of hydrogen bromide.

(c) Thermal decomposition of organic bromides

(i) The nature of the decompositions

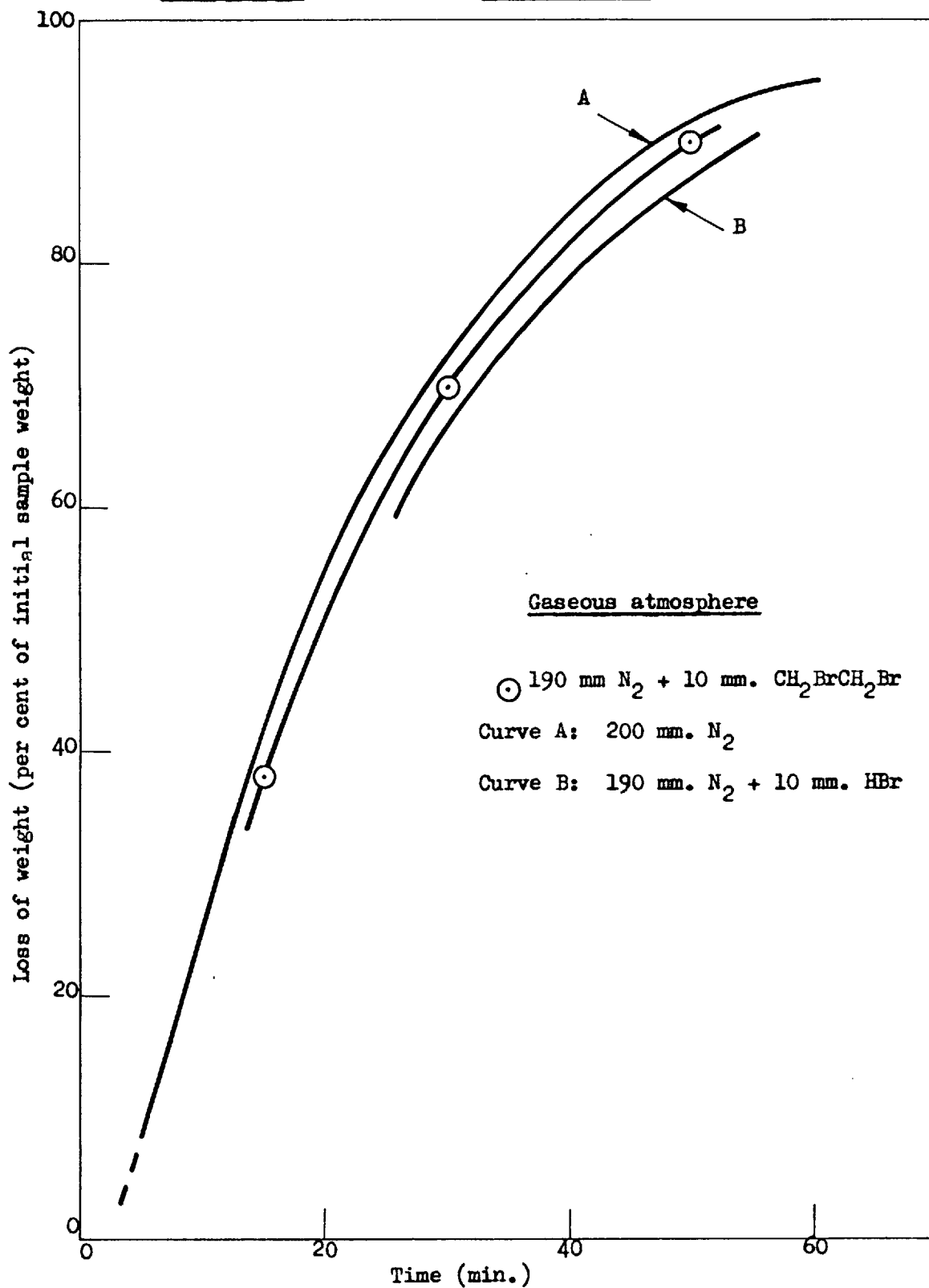
It was noted that, if bromoethane was introduced into the reaction vessel at 430°C in the absence of polymer, a readily

Figure 32

Loss of weight of polyethylene during pyrolysis showing
the influence of 1,2-dibromoethane

Temperature: 430°C

Sample weight: 5 mg.



measureable pressure increase was observed. This was clearly due to the well-known decomposition of bromoethane to give ethylene and hydrogen bromide.

For each of the bromides used, mixtures containing 40 mm. of the bromide and 160 mm. of nitrogen were introduced to the reaction vessel at zero time and samples were withdrawn after 30 minutes for analysis, by gas chromatography, of the hydrocarbon products. The results shown in table 20 suggest that, for the monobromoalkanes (excluding bromomethane) the decomposition involves the elimination of hydrogen bromide. In the case of 1,2-dibromoethane, it was concluded that decomposition involved the elimination of only one molecule of hydrogen bromide per molecule of dibromide, since no hydrocarbons were present in the reaction products.

(ii) The rates of decomposition of the bromides

On the assumption that where decomposition occurred it involved the elimination of one molecule of hydrogen bromide per molecule of organic bromide originally present, the percentage decomposition was deduced from measurements of pressure change. No noticeable pressure increase was observed on the introduction of a bromomethane + nitrogen mixture into the reaction vessel. The estimated extents of decomposition of the monobromoalkanes are shown in figure 33. It was found that the pressure increase was in all cases unaffected by the presence of a 5 mg. sample of polyethylene in the reaction vessel. Gas chromatographic analysis was also employed to follow the concentrations of bromomethane and bromoethane in the reaction vessel.

Table 20

Hydrocarbon products from the decomposition of organic bromides

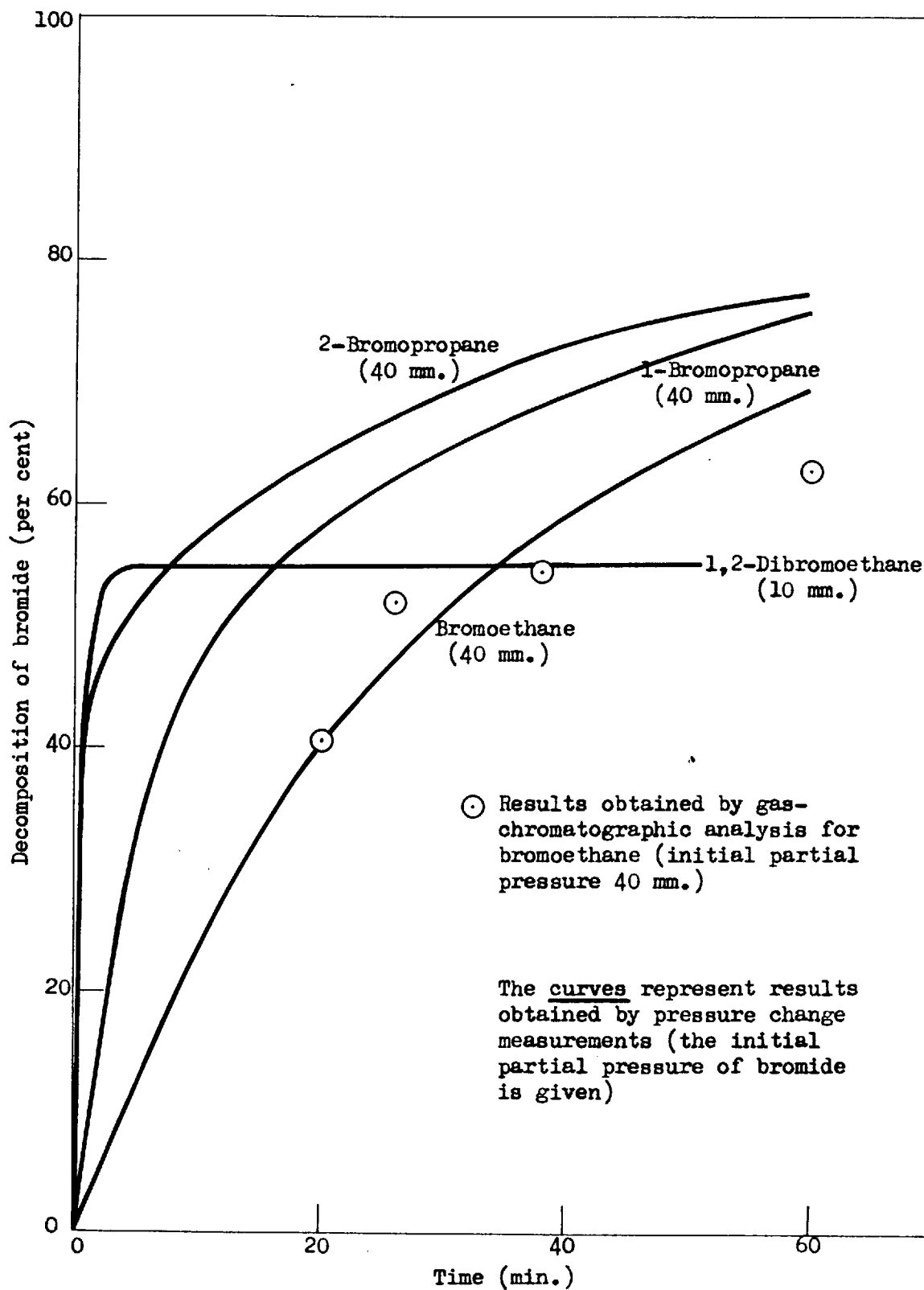
Temperature : 430°C

Compound	Hydrocarbon
Bromomethane	Methane (trace)
Bromoethane	Ethylene
1-Bromopropane	Propene
2-Bromopropane	Propene
1,2-Dibromoethane	None

Figure 33

Thermal decomposition of organic bromides in the reaction vessel system

Temperature: 430°C Total initial pressure (with N₂): 200 mm.



No appreciable decrease in the concentration of bromomethane was observed. The values obtained for the concentration of residual bromoethane are shown as points in figure 33; the results are reasonably consistent with those obtained by measurements of pressure change.

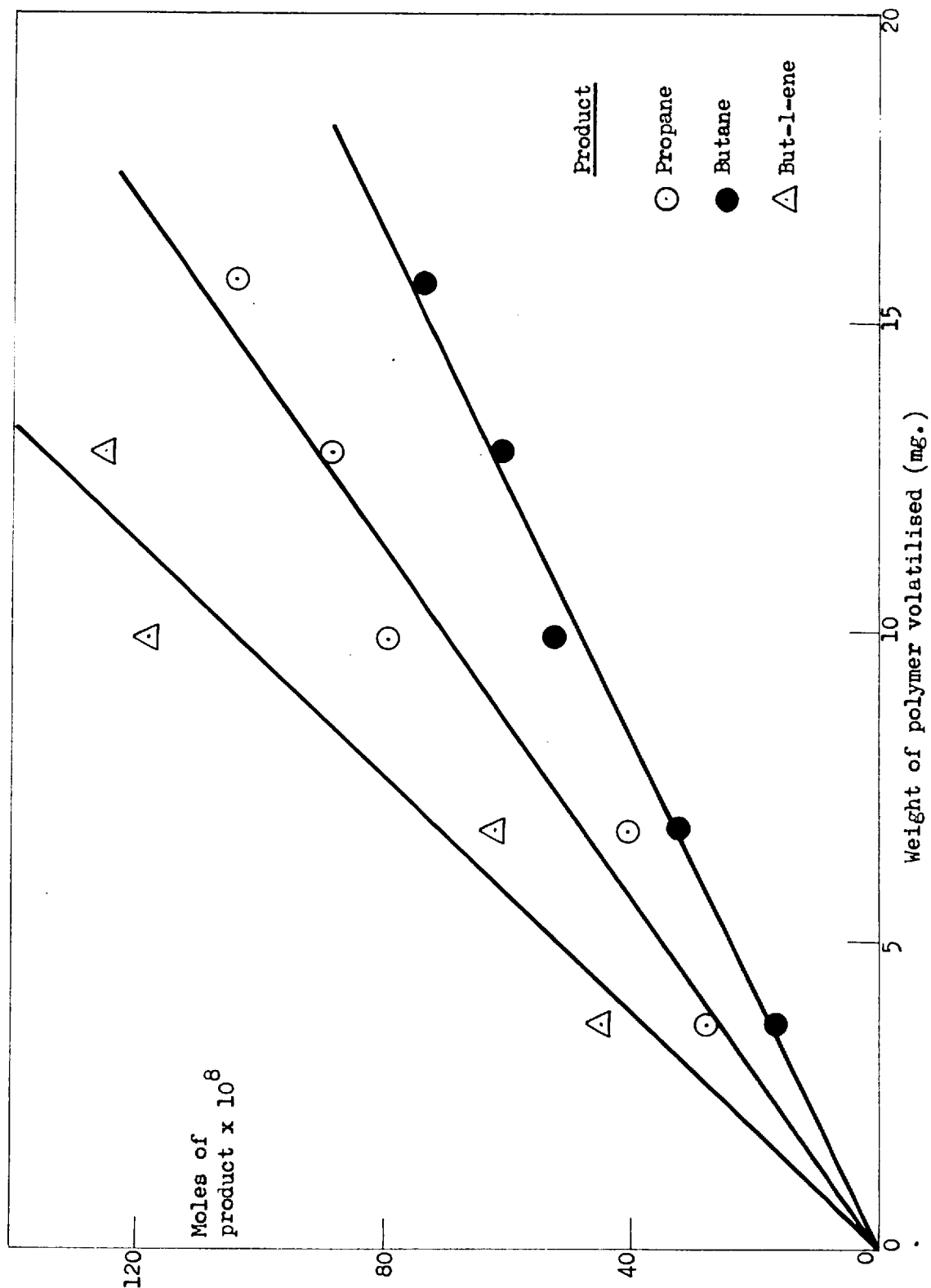
The results shown in figure 33 do not give an accurate indication of the extent of the decomposition, and hence the corresponding concentration of hydrogen bromide, in the reaction vessel since a significant quantity of the gas in the system (that in the introduction tube) is below the temperature of the reaction vessel. However, the conclusion may be drawn from these results that, for the monobromoalkanes, the rate of decomposition (and hence the rate of liberation of hydrogen bromide) decreased in the order 2-bromopropane > 1-bromopropane > bromoethane > bromomethane. For 1,2-dibromoethane the decomposition appeared to be quite rapid and the final extent of the breakdown was consistent with the elimination of approximately one molecule of hydrogen bromide from one molecule of the additive (figure 33).

5. Analysis of the volatile products of degradation

(a) Influence of sample size

Analyses were made of the products formed during pyrolysis of polyethylene at 430°C in an atmosphere of nitrogen using sample weights varying from 5 to 25 mg. In each case pyrolysis was continued for 30 minutes and the loss of weight occurring during each run was determined. In figure 34 the numbers of moles of three of the most abundant products are plotted against the weight of the polymer volatilised. The

Figure 34



Influence of sample weight on the formation of volatile products during the pyrolysis of polyethylene

Temperature: 430 °C Atmosphere: 200 mm. N₂ Pyrolysis time: 30 min.

quantity of each product was found to be approximately proportional to the weight of the polymer decomposed. This relationship was found to exist for all the volatile pyrolysis products of the polymer.

(b) Nature of the volatile products

Samples of the volatile products, obtained after 50 mg. samples had been pyrolysed for 10, 20 and 30 minutes, were withdrawn and analysed. A complex mixture of C_2 - C_7 hydrocarbons was obtained and the main constituents are listed in table 21. Here the amount of each product which was obtained in sufficient quantities for estimation is expressed in two ways. First the total number of moles of each product was summed and the moles of each product was then expressed as a percentage of this sum. Secondly the weight of each product was expressed as a percentage of the weight of the polymer volatilised. The values given in table 21 are mean values obtained from the three runs (described above) with 50 mg. samples. Ethane and ethylene were not sufficiently well resolved in the gas chromatographic analysis for separate values to be obtained. The figures given in table 21 are derived from the sum of the quantities of these two products obtained by the use of a mean sensitivity in the peak area calculation and a mean molecular weight.

No oxygenated hydrocarbons were detected in the volatile products of pyrolysis.

(c) Influence of hydrogen bromide

Samples of the volatile products were withdrawn after various times during the pyrolysis of 5 mg. samples of the polymer at 430 and 400°C and in different gaseous atmospheres. The pyrolysis in helium was investigated so that the effect of hydrogen bromide could be compared

Table 21

Analysis of the C_2-C_7 fraction of products formed during
pyrolysis of polyethylene

Temperature: 430°C Atmosphere: 200mm. N_2 Sample weight: 50 mg.

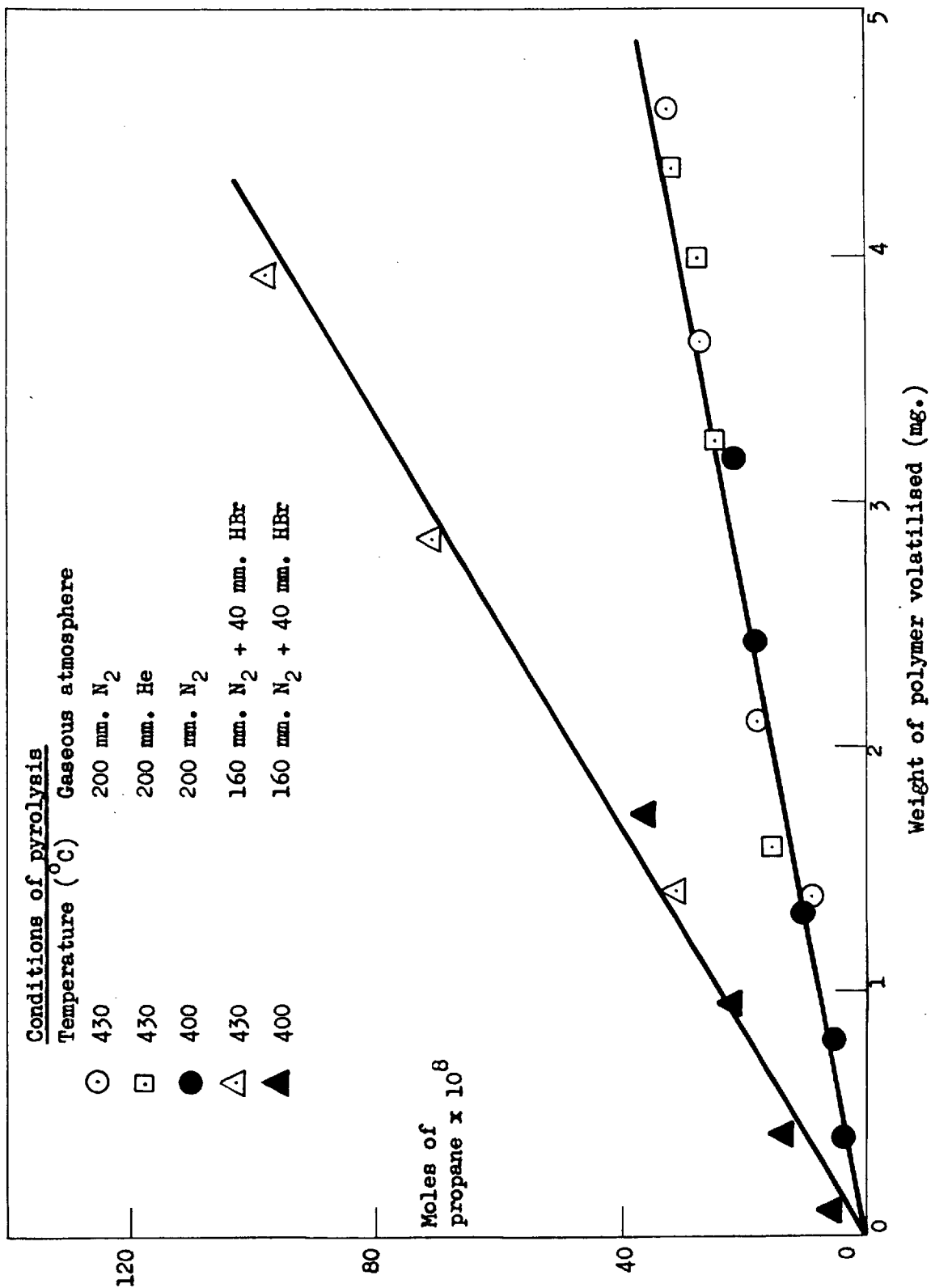
Product	Mole per cent of C_2-C_7 fraction	Weight per cent of pyrolysed part
Ethane + Ethylene	34.4	0.59
Propane	10.2	0.26
Propene	14.7	0.36
Butane	6.8	0.23
But-1-ene	11.7	0.39
But-2-ene(trans)	0.9	0.03
But-2-ene (cis)	0.6	0.02
Pentane	2.7	0.12
Pent-1-ene	4.7	0.19
Hexane	1.3	0.07
Hex-1-ene	4.8	0.24
Hex-2-ene (trans)	2.1	0.10
Heptane	2.5	0.15
Hept-1-ene	2.6	0.15
Total	100.0	2.90

with that of the nature of the inert gas. The numbers of moles of some typical products are plotted against the weights of polymer volatilised in figures 35-40. The general conclusions drawn from the results obtained may be summarised as follows.

The number of moles of each product obtained in sufficient quantity for quantitative analysis was found to be approximately proportional to the weight of polymer volatilised (except in the case of propene). Thus the quantity of each product formed could be expressed as moles per mg. of polymer volatilised and hereafter in this section this quantity will be called the 'yield' of the product.

Reference to figures 35-40 shows that the yields of the products during pyrolysis in nitrogen at 400 and 430°C and in helium at 430°C were approximately the same. The mean yields of given products obtained under these three sets of conditions are given in table 22. The yields of given products obtained during pyrolysis in the nitrogen + hydrogen bromide mixture at 400°C were substantially the same as the yields in an identical atmosphere at 430°C and the mean values of the yields obtained at these two temperatures are given in table 22. The ratios of the yields of given products resulting from pyrolysis of polyethylene in hydrogen bromide to the yields of those same products formed during pyrolysis in a pure inert gas are also given in table 22.

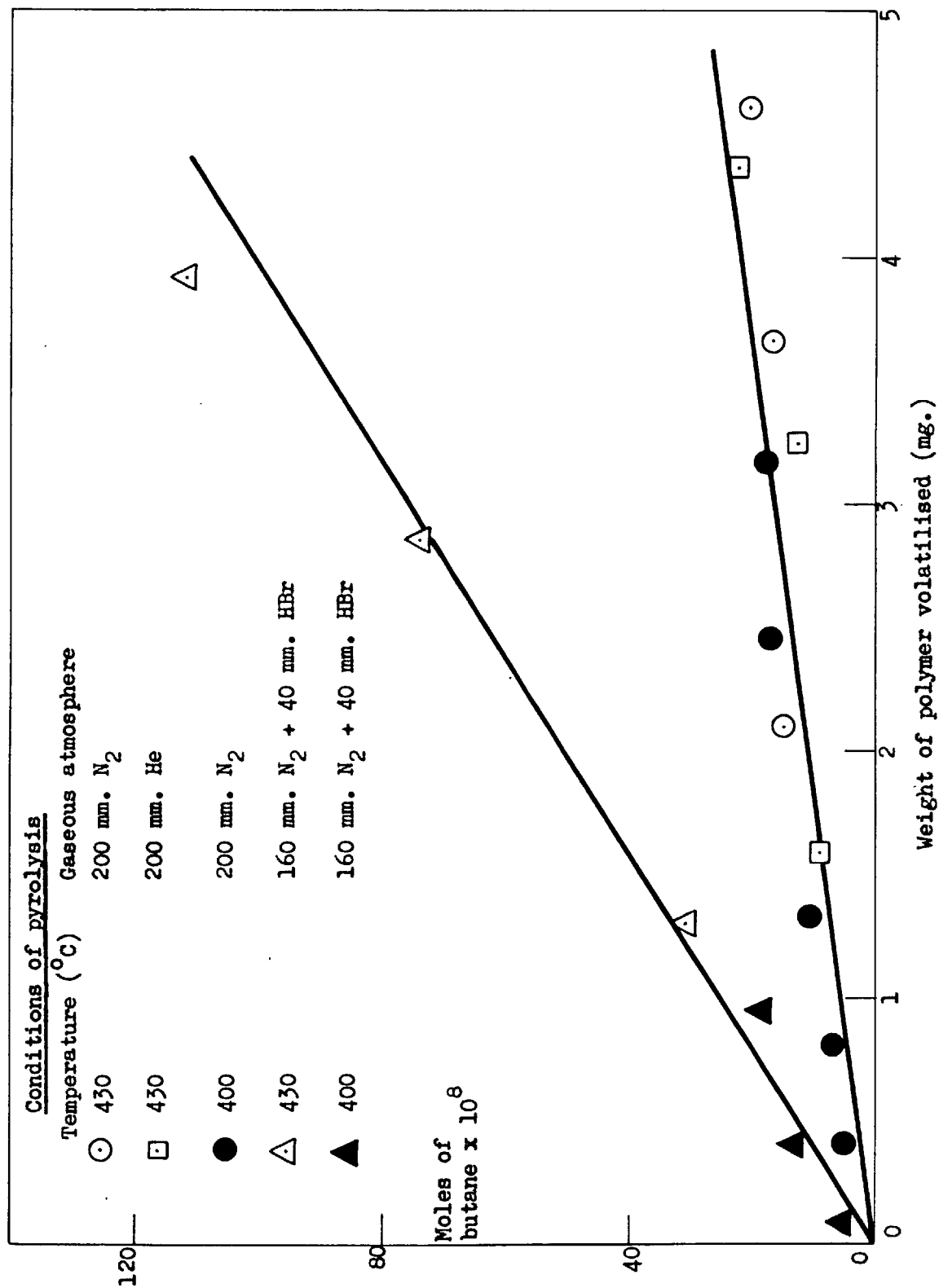
It was found that the yields of propane, butane and pentane were increased by the presence of hydrogen bromide, the increase being the greatest for pentane and the smallest for propane. Hydrogen bromide increased also the yields of the but-2-enes. On the other hand, the



Formation of propane during pyrolysis of polyethylene showing influence of gaseous atmosphere

Sample weight: 5 mg.

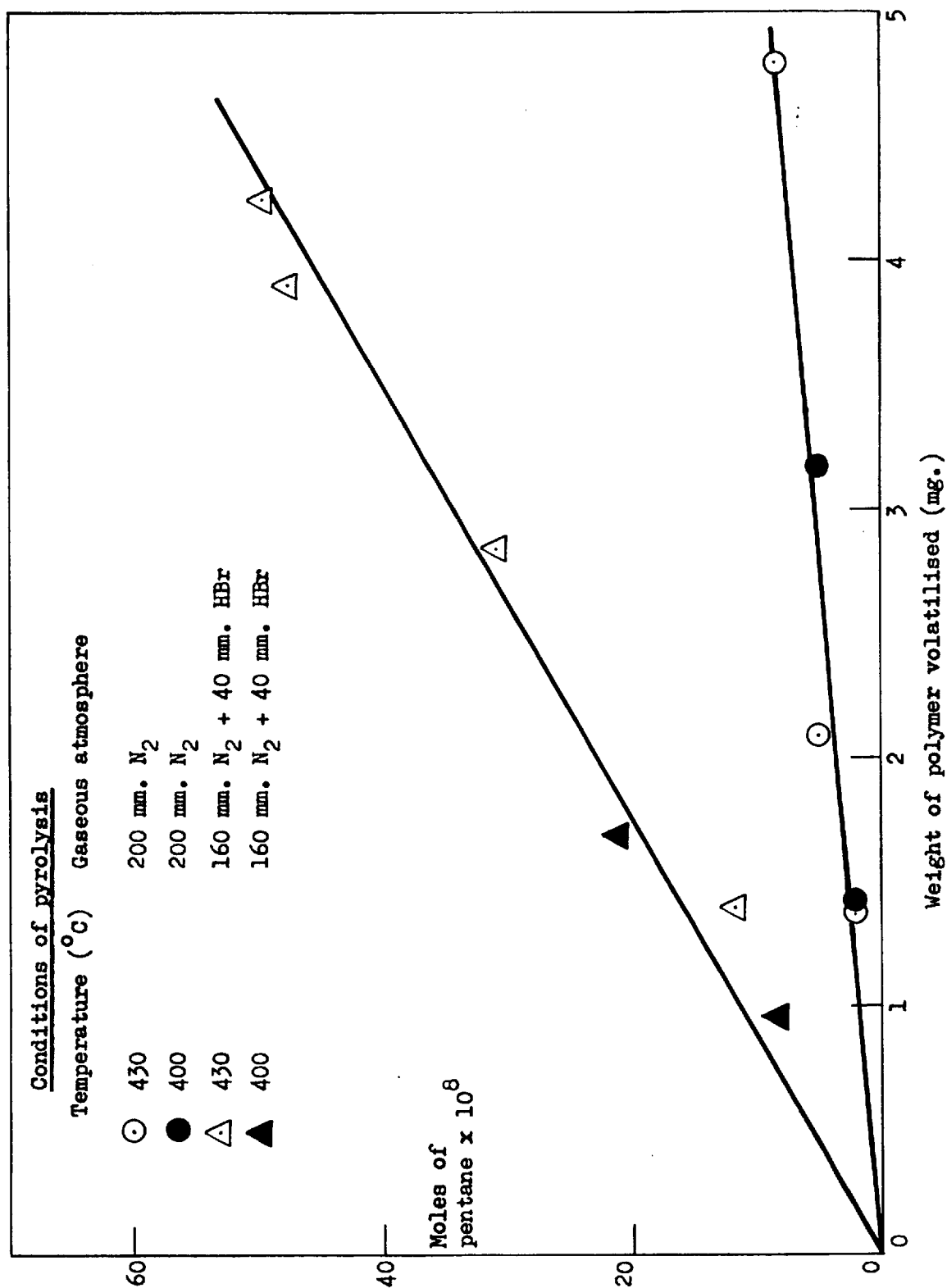
Figure 36



Formation of butane during pyrolysis of polyethylene showing influence of gaseous atmosphere

Sample weight: 5 mg.

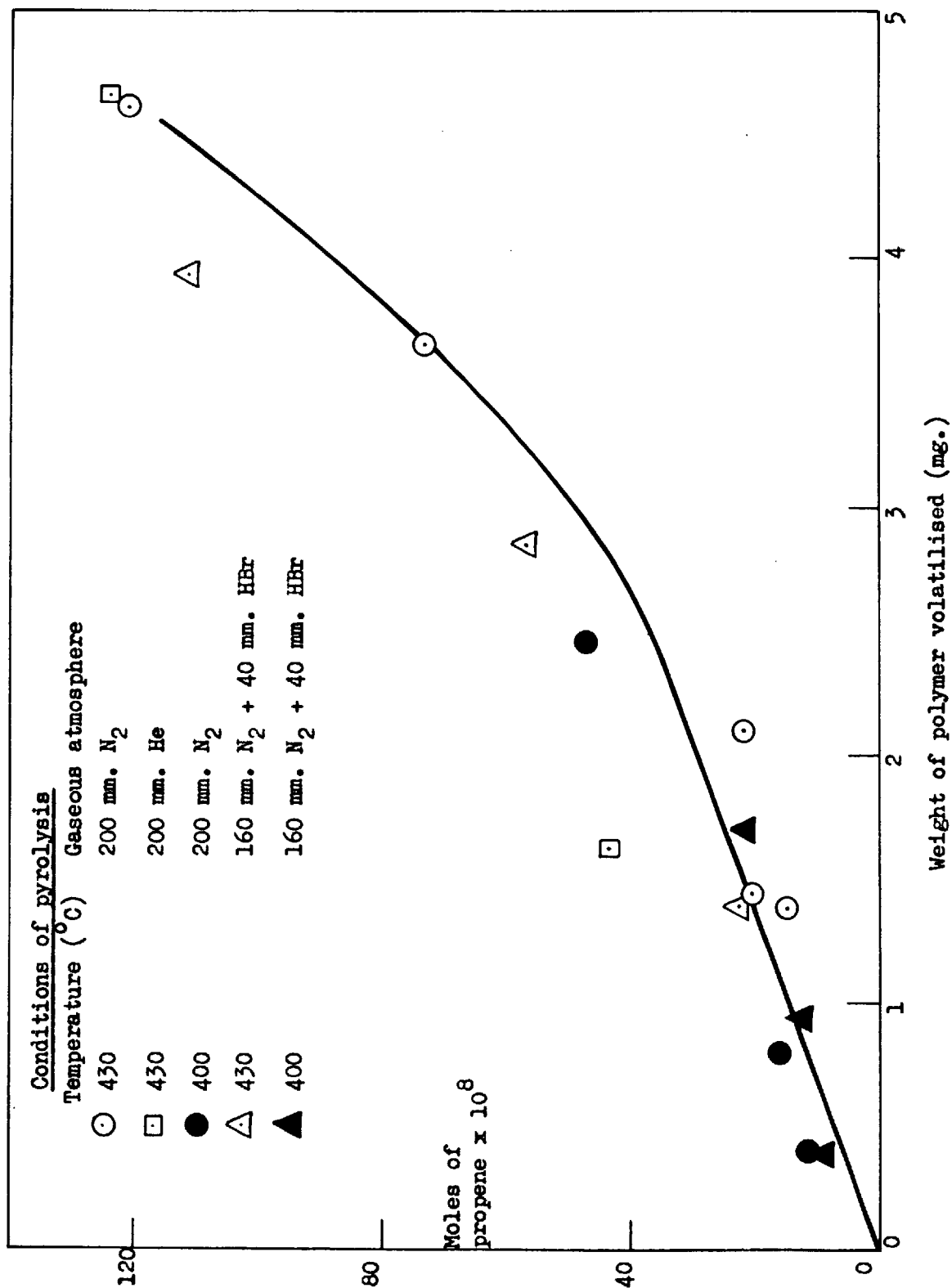
Figure 37



Formation of pentane during pyrolysis of polyethylene showing influence of gaseous atmosphere

Sample weight: 5 mg.

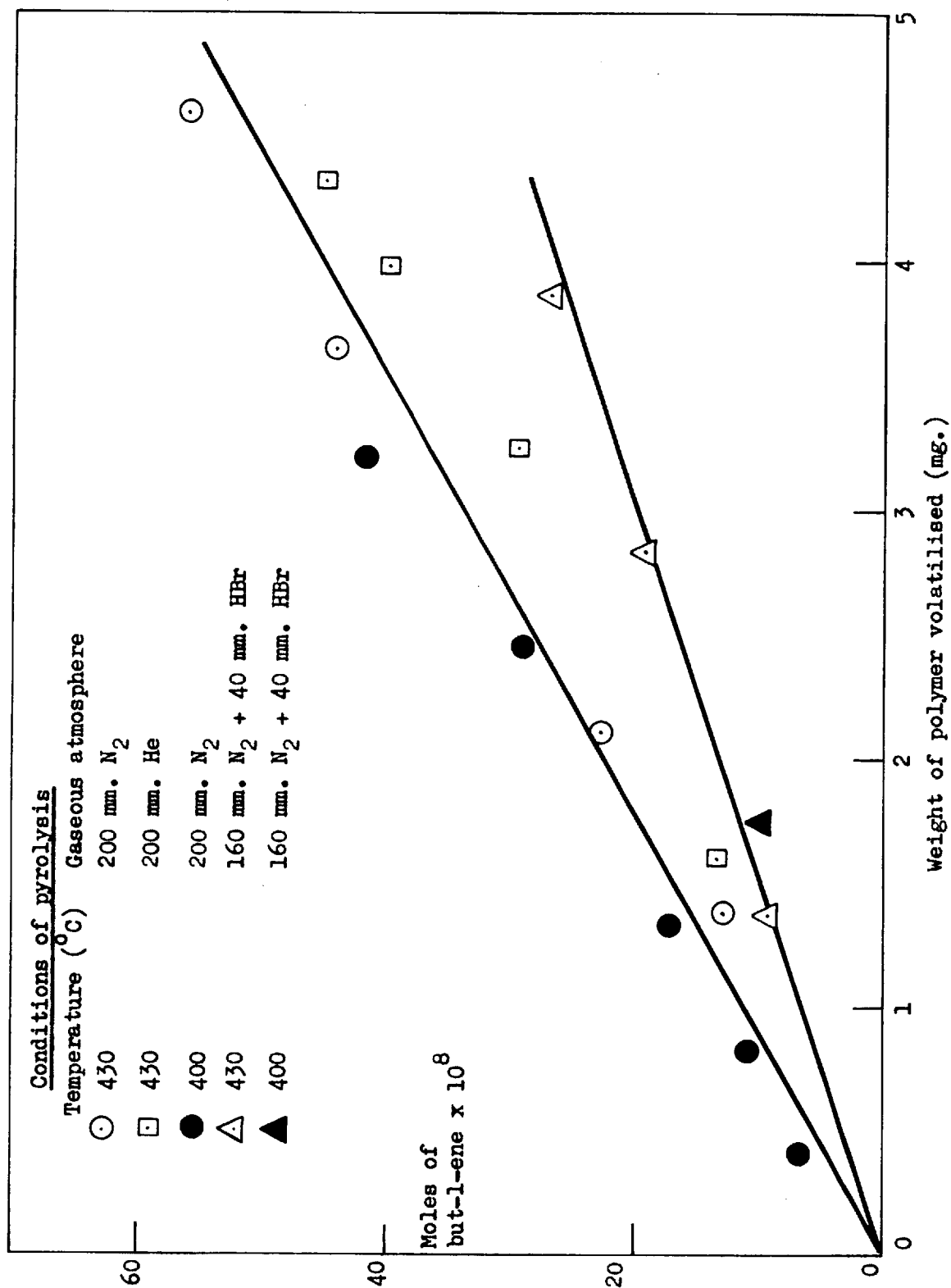
Figure 38



Formation of propene during pyrolysis of polyethylene showing influence of gaseous atmosphere

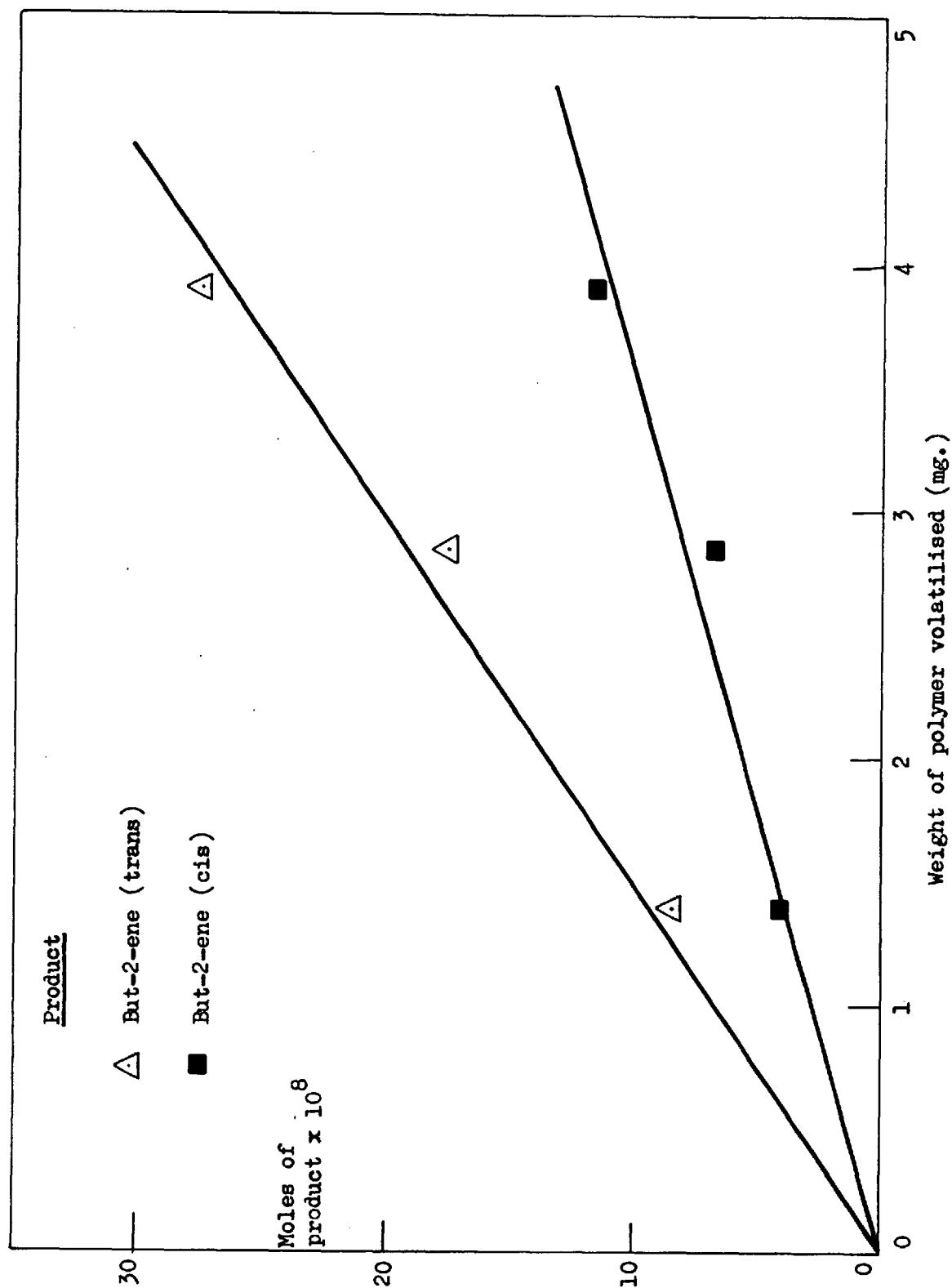
Sample weight: 5 mg.

Figure 39



Formation of but-1-ene during pyrolysis of polyethylene showing influence of gaseous atmosphere

Sample weight: 5 mg.



Formation of the but-2-enes during pyrolysis of polyethylene

Temperature: 430°C

Sample weight: 5 mg.

Gaseous atmosphere: 160 mm. N₂ + 40 mm. HBr

Table 22

Influence of hydrogen bromide on the quantities of products formed during the pyrolysis of polyethylene

Sample weight : 5 mg.

Other conditions given by :

- | | | | |
|---|--------------------------------|---|---|
| a | 200 mm. N ₂ , 430°C | d | 160 mm. N ₂ +40 mm. HBr, 430°C |
| b | 200 mm. He , 430°C | e | 160 mm. N ₂ +40 mm. HBr, 400°C |
| c | 200 mm. N ₂ , 400°C | | |

Product	Quantity of product (mole x 10 ⁸ per mg. weight loss of polymer sample)		Ratio of quantity in column 2 to that in column 1
	1. Mean for condi- tions a,b,c	2. Mean for con- ditions d,e	
Propane	7.5	23.9	3.2
Butane	5.6	25.2	4.5
Pentane	1.8	11.5	6.6
Propene	16.6	16.6	1.0
But-1-ene	11.8	6.6	0.56
But-2-ene (trans)	small	6.8	>1.0
But-2-ene (cis)	small	2.8	>1.0

production of but-1-ene was decreased by hydrogen bromide. The yield of propene appeared to be unaffected by hydrogen bromide. It was also observed that, for the latter product alone, the yield, although it remained constant for the initial stages of the reaction, eventually increased with the extent of pyrolysis (figure 38).

From this work the conclusion may be drawn that the quantity of a given product formed during pyrolysis in a given gas or gas mixture is unaffected by temperature and depends only on the weight of the polymer volatilised. Hydrogen bromide does not influence the nature of the volatile products formed (no brominated hydrocarbons were detected in the products of pyrolysis) although this additive does influence the relative yields of these products. A further investigation of the latter effect is described below.

(d) Gas phase degradation of the volatile products and the influence of hydrogen bromide thereon

Using 150 mg. samples, four runs were carried out with the reaction vessel at 430°C. The conditions were as follows.

(A) After 10 minutes' pyrolysis in 100 mm. of nitrogen the polymer sample was withdrawn and a sample of the pyrolysis products was taken for analysis.

(B) After 10 minutes' pyrolysis in 100 mm. of nitrogen the polymer sample was withdrawn. The products were allowed to remain in the reaction vessel for a further 15 minutes when a sample of the products was taken.

(C) After 10 minutes' pyrolysis in an atmosphere containing 20 mm. of hydrogen bromide + 80 mm. of nitrogen the polymer sample was withdrawn and a sample of the pyrolysis products was taken.

(D) After 10 minutes' pyrolysis in 90 mm. of nitrogen the polymer sample was withdrawn. After 5 minutes, 20 mm. of hydrogen bromide were introduced into the reaction vessel and a sample of the products was taken after a further 10 minutes.

The quantities of the products obtained in these runs are expressed as moles per mg. of polymer volatilised in table 23. Pyrolysis in an atmosphere containing hydrogen bromide increased markedly the yields of alkanes and alk-2-enes per mg. of polymer volatilised compared with pyrolysis in an atmosphere containing only nitrogen (compare A and C). On the basis of the same comparison the yields of propene, but-1-ene and pent-1-ene increased slightly, while those of hex-1-ene and hept-1-ene decreased.

A similar pattern of change in the quantities of products obtained is apparent if the values in columns B and D in table 23 are compared. Thus, when hydrogen bromide was introduced into the reaction vessel containing the products of pyrolysis (column D) the yields of the alkanes and alk-2-enes increased noticeably; there was, however, a smaller increase, or in some cases a decrease, in the yields of the alk-1-enes compared with a similar run in which no hydrogen bromide was present (column B). It is evident, therefore, that the redistribution of products in the C_2-C_7 fraction which is observed in experiments where polyethylene is degraded in the presence of hydrogen bromide also occurs in the direct reaction between hydrogen bromide and the volatile degradation products of the polymer.

From the total yields of the C_2-C_7 fraction obtained under conditions A, B, C and D (table 23) it is concluded that the volatile

Table 23

The extent of pyrolysis of the degradation products of polyethylene and the influence of hydrogen bromide on this reaction

Temperature : 430°C

Sample weight : 150 mg.

Product	Quantity (Moles x 10 ⁸ per mg. weight loss of polymer sample)			
	A*	B*	C*	D*
Ethane + Ethylene	20.1	46.8	37.2	66.2
Propane	9.8	11.0	18.8	26.1
Propene	10.0	15.6	14.0	32.5
Butane	6.7	7.8	15.6	16.4
But-1-ene	10.2	13.7	12.6	13.1
But-2-ene (trans)	0.6	1.3	5.6	8.3
But-2-ene (cis)	0.4	0.9	3.6	5.9
Pentane	2.2	2.3	5.3	6.9
Pent-1-ene	2.9	4.8	3.7	4.7
Pent-2-ene (trans)	trace	trace	2.0	3.9
Pent-2-ene (cis)	trace	trace	0.9	2.1
Hexane	0.7	1.1	1.8	3.3
Hex-1-ene	2.8	4.9	2.2	3.8
Heptane	1.4	2.1	2.1	3.4
Hept-1-ene	1.1	2.2	trace	1.9
Total	68.9	114.5	125.4	198.5

* The procedure adopted to obtain the results shown in columns A,B, C and D is described on pages 156 and 157.

products formed directly by the degradation of the polymer undergo further pyrolysis in the reaction vessel and that the presence of hydrogen bromide increases the rate of this secondary reaction.

Other data obtained from these experiments, i.e. the weight loss after 10 minutes' pyrolysis and the quantity of the C_2-C_7 fraction expressed as the weight per cent of polymer degraded, are given in table 24. Hydrogen bromide reduced the loss of weight but increased the weight per cent of the C_2-C_7 fraction of volatile products.

6. Pressure increase measurements

The pressure change accompanying the pyrolysis of 150 mg. samples of polyethylene was investigated. The results obtained from experiments involving the pyrolysis of the polymer in nitrogen and in a nitrogen + hydrogen bromide mixture are shown in figure 41, where the pressure increase, after a given pyrolysis time, is plotted against the corresponding loss of weight of the polymer sample. In the presence and absence of hydrogen bromide the pressure increase was approximately proportional to the weight of the polymer volatilised. For a given loss of weight of polymer, however, the pressure increase was greater in the presence of hydrogen bromide than in its absence. Values of the pressure increase corresponding to a polymer weight loss of one mg. were calculated from the lines drawn in figure 41 and the values obtained are given in table 24. By calibration of the reaction vessel system at 430°C by means of the standard volume vessel, it was possible to calculate the increase in the number of moles of gas in the system corresponding to a given pressure increase. It was thus possible to find the increase in the sum total number of moles of all products,

Table 24

Influence of hydrogen bromide on the quantity of volatile product produced by the pyrolysis of polyethylene

Temperature : 430°C

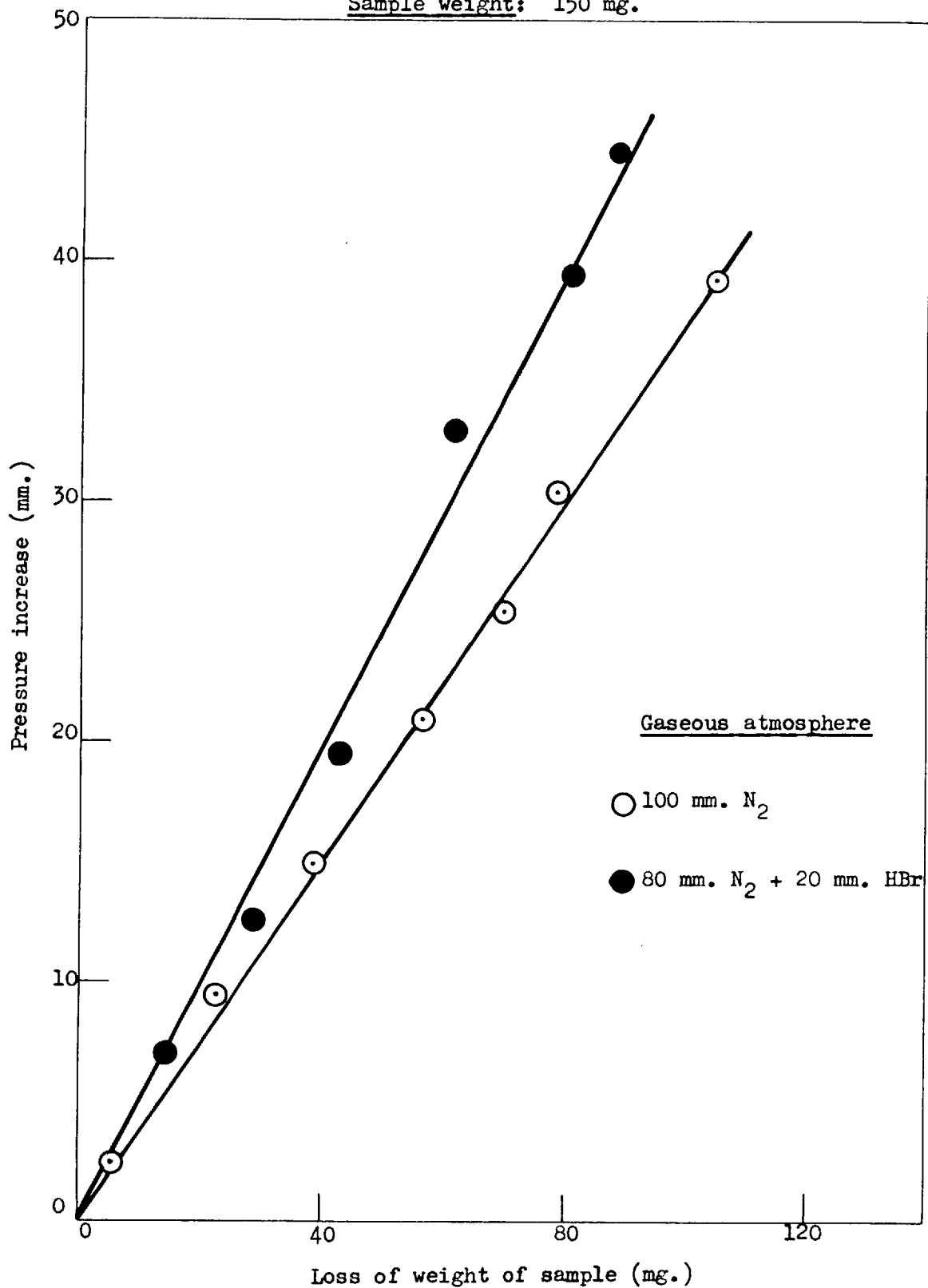
Sample weight: 150 mg.

Gaseous atmosphere	100 mm. N ₂	20 mm. HBr + 80 mm. N ₂
Weight lost after 10 min. pyrolysis (mg.)	22	14
Pressure increase (mm. per mg. volatilised)	0.375	0.492
Total volatile product (moles per mg. volatilised)	4.73×10^{-6}	6.20×10^{-6}
C ₂ - C ₇ product (moles per mg. volatilised)	0.69×10^{-6}	1.25×10^{-6}
C ₂ - C ₇ product (mole per cent of total volatile product)	14.5	20.2
C ₂ - C ₇ product (weight per cent of total volatile product)	3.3	5.9

Figure 41

Pressure change accompanying the pyrolysis of polyethylene
showing the influence of hydrogen bromide

Sample weight: 150 mg.



volatile at the temperature of pyrolysis, accompanying the volatilisation of one mg. of polymer. The figures thus obtained for the pyrolysis of the polymer in the presence and absence of hydrogen bromide are given in table 24, which also shows the number of moles of C_2-C_7 products (obtained from columns A and C of table 23) expressed both as a total, per mg. of polymer volatilised, and as a percentage of the total number of moles of all volatile products formed. The effect of hydrogen bromide was to increase the proportion of C_2-C_7 hydrocarbon molecules in the pyrolysis products.

C The oxidation of polyethylene

1. Pressure change measurements

(a) Influence of sample size

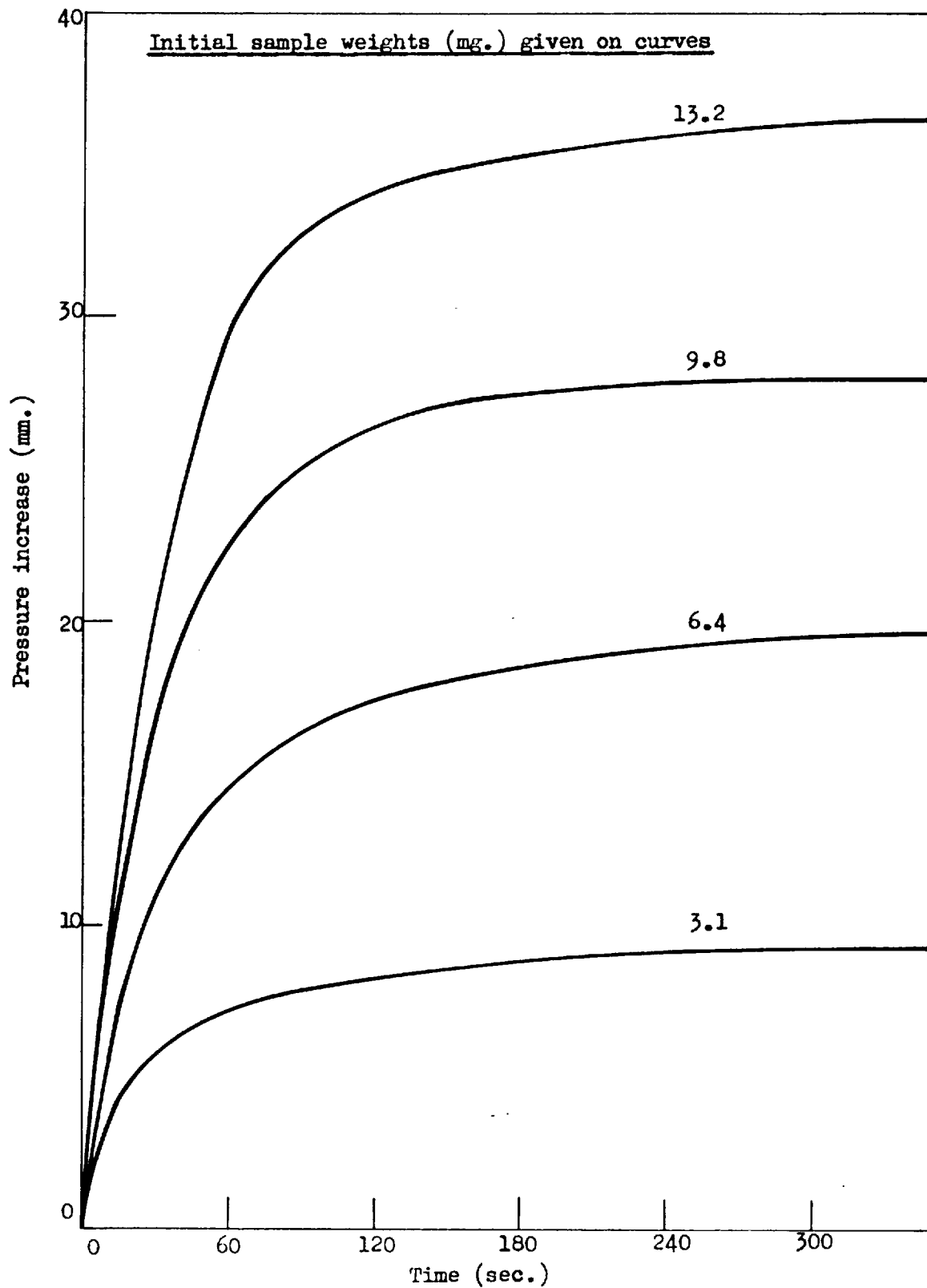
In all the experiments involving the oxidation of polyethylene the oxygen was introduced into the reaction vessel after the polymer had been undergoing pyrolysis under vacuum for exactly ten minutes. The reaction vessel was pumped continuously during this ten minute period so that all the volatile products formed during the pyrolysis of the polymer were removed. The weights of the polymer remaining after ten minutes' pyrolysis under these conditions were determined for varying weights of polymer initially introduced so that it was known what weight of polymer was present at the instant at which oxygen was introduced. The pressure increase curves were then determined for constant oxygen pressure and constant total pressure for varying sample weights. Some typical plots of pressure increase against time are shown in figure 42. In the presentation of these and subsequent

Figure 42

Influence of initial sample weight on the pressure change accompanying the oxidation of polyethylene

Temperature: 430°C

Initial gaseous atmosphere: 150 mm. O₂
+50 mm. N₂



pressure change curves the zero of the time scale is taken as the instant at which oxygen was admitted to the reaction vessel and the polymer weights given are the weights present in the boat at the instant at which oxygen was introduced.

In all cases the pressure eventually attained a constant value. This was reached within 300 seconds except for the largest polymer sample used (13.2 mg.). In figure 43 the final pressure increase is plotted against the weight of polymer present when the oxygen was introduced. It will be seen that this pressure increase is proportional to the weight of polymer sample used.

The weight of the residue from each of the experiments was determined, the residue was reintroduced into the reaction vessel and 200 mm. of oxygen was added. No further pressure change was observed and when the residue was reweighed, it was found that no change in weight had occurred. Thus it was concluded that oxidation was complete for all the sample weights investigated.

The pressure increase after 5 and 15 seconds' oxidation is plotted against the weight of polymer sample in figure 44. The pressure increase for a given time interval for different weights of polymer gives an indication of the influence of sample weight on the initial rate of pressure increase. The pressure increase is approximately proportional to the weight of sample up to a sample size of about 8 mg. For larger sample weights the pressure increase, per mg. of polymer sample, decreases.

(b) Influence of initial oxygen concentration

The course of the oxidation of a polymer sample, of constant

Figure 43

Influence of initial sample weight on the final pressure increase recorded after oxidation of polyethylene

Temperature: 430°C Initial gaseous 150 mm. O₂
atmosphere : +50 mm. N₂

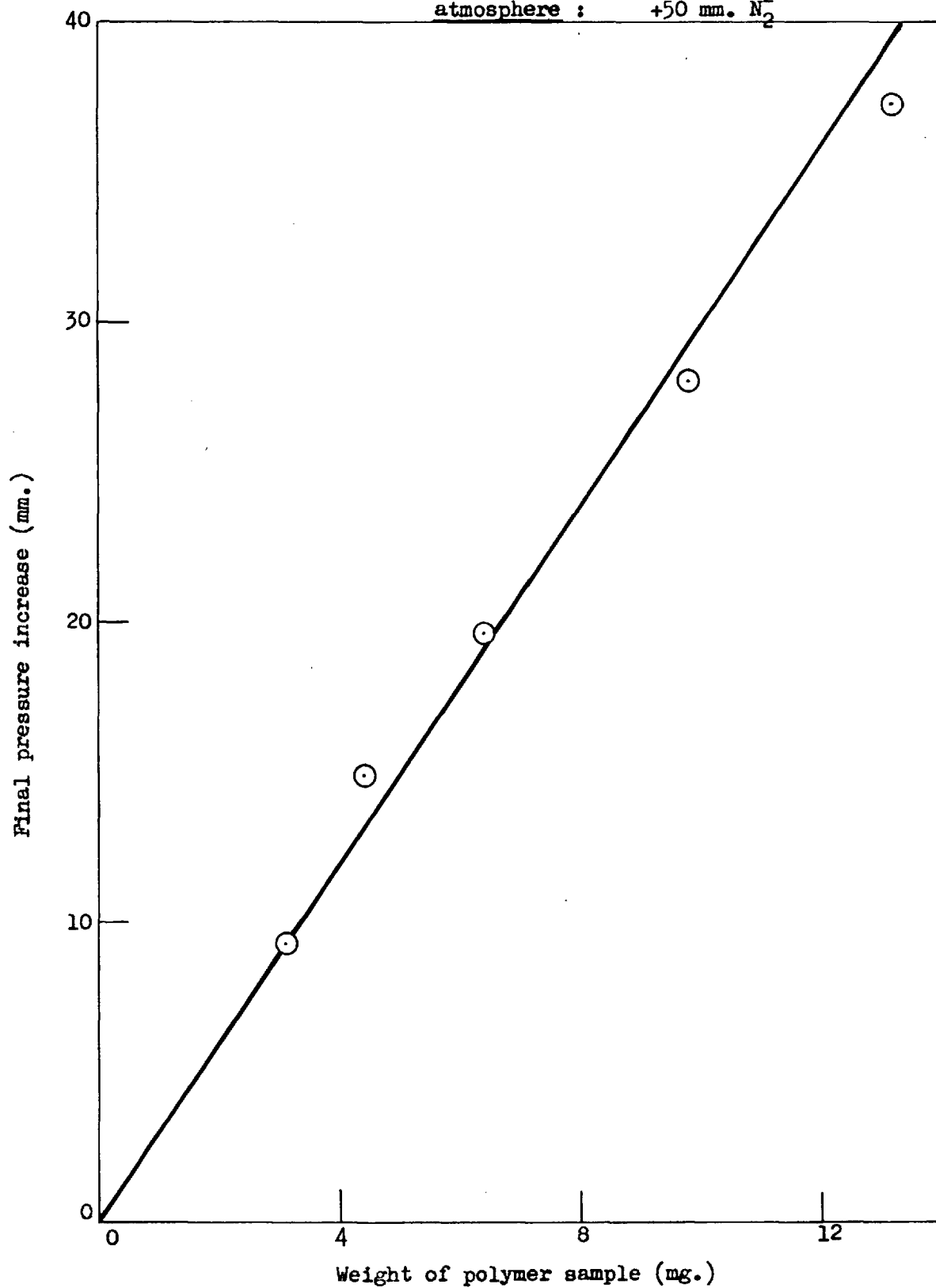
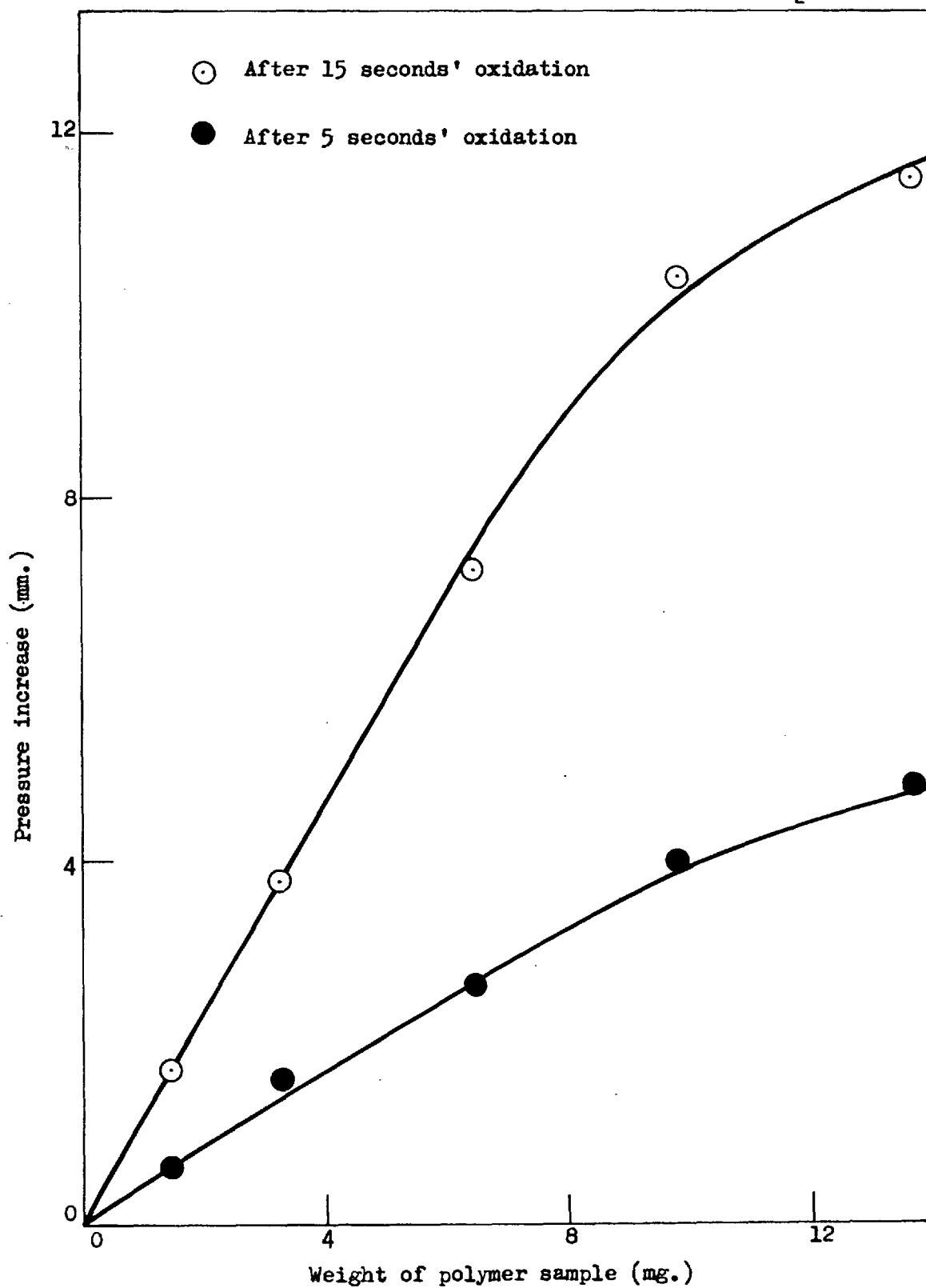


Figure 44

Influence of initial sample weight on the rate of pressure increase during the oxidation of polyethylene

Temperature: 430°C

Initial gaseous atmosphere : 150 mm. O₂
+50 mm. N₂



weight, was followed using varying initial pressures of oxygen. The total initial pressure in the system was maintained constant by the addition of nitrogen. Some results from these experiments are shown in figure 45. The pressure increase after 5 and 15 seconds' oxidation is plotted against the pressure of oxygen used in figure 46. The pressure increase varies linearly with initial oxygen concentration over the whole range investigated.

(c) Influence of hydrogen bromide

A series of runs was carried out using a constant weight of polymer sample and a constant oxygen pressure but with varying pressures of hydrogen bromide present. The total pressure of gas added to the system was kept constant using nitrogen. Some typical pressure-time curves for different hydrogen bromide concentrations are shown in figure 47. The pressure increases observed after 5 and 15 seconds' oxidation are plotted against the concentration of hydrogen bromide in figure 48. In all cases the presence of hydrogen bromide increased the rate of pressure rise. The maximum increase in rate was found to occur with about 5 mm. of hydrogen bromide present.

It was found that, during oxidation in the presence of hydrogen bromide, the pressure reached a maximum value and subsequently decreased approximately linearly with time. The maximum pressure increase, the time at which it was observed and the pressure increase after 300 seconds' oxidation for different partial pressures of hydrogen bromide are given in table 25. The maximum pressure increase was observed in most cases after about 90 seconds. The subsequent decrease was larger, the greater the concentration of hydrogen bromide.

Figure 45

Influence of initial oxygen concentration on the pressure change accompanying the oxidation of polyethylene

Temperature: 430°C

Sample weight: 6.4 mg.

Initial total pressure (with N₂): 200 mm.

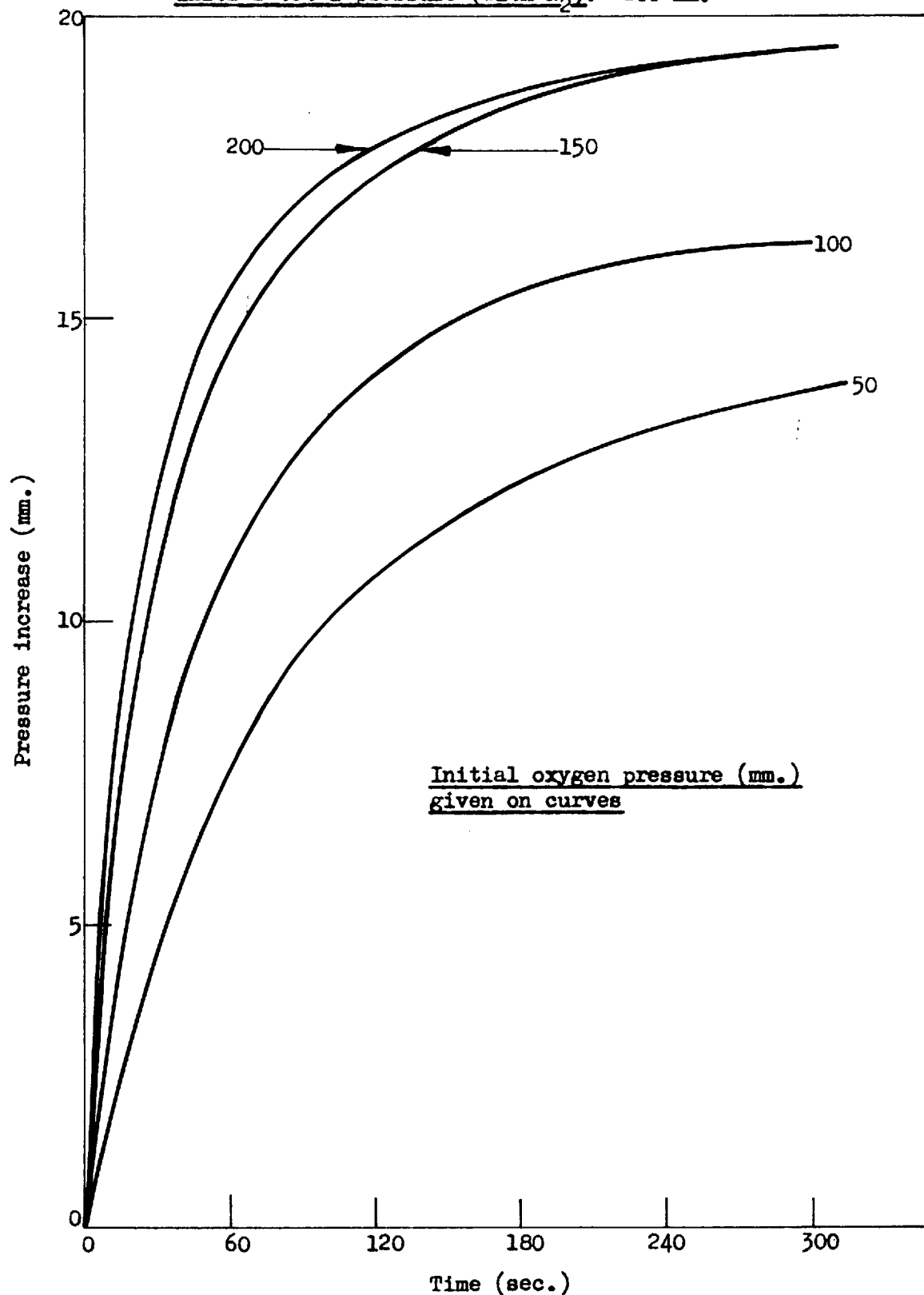


Figure 46

Influence of initial oxygen concentration on the rate of pressure increase during the oxidation of polyethylene

Temperature: 430°C

Sample weight: 6.4 mg.

Initial total pressure (with N₂): 200 mm.

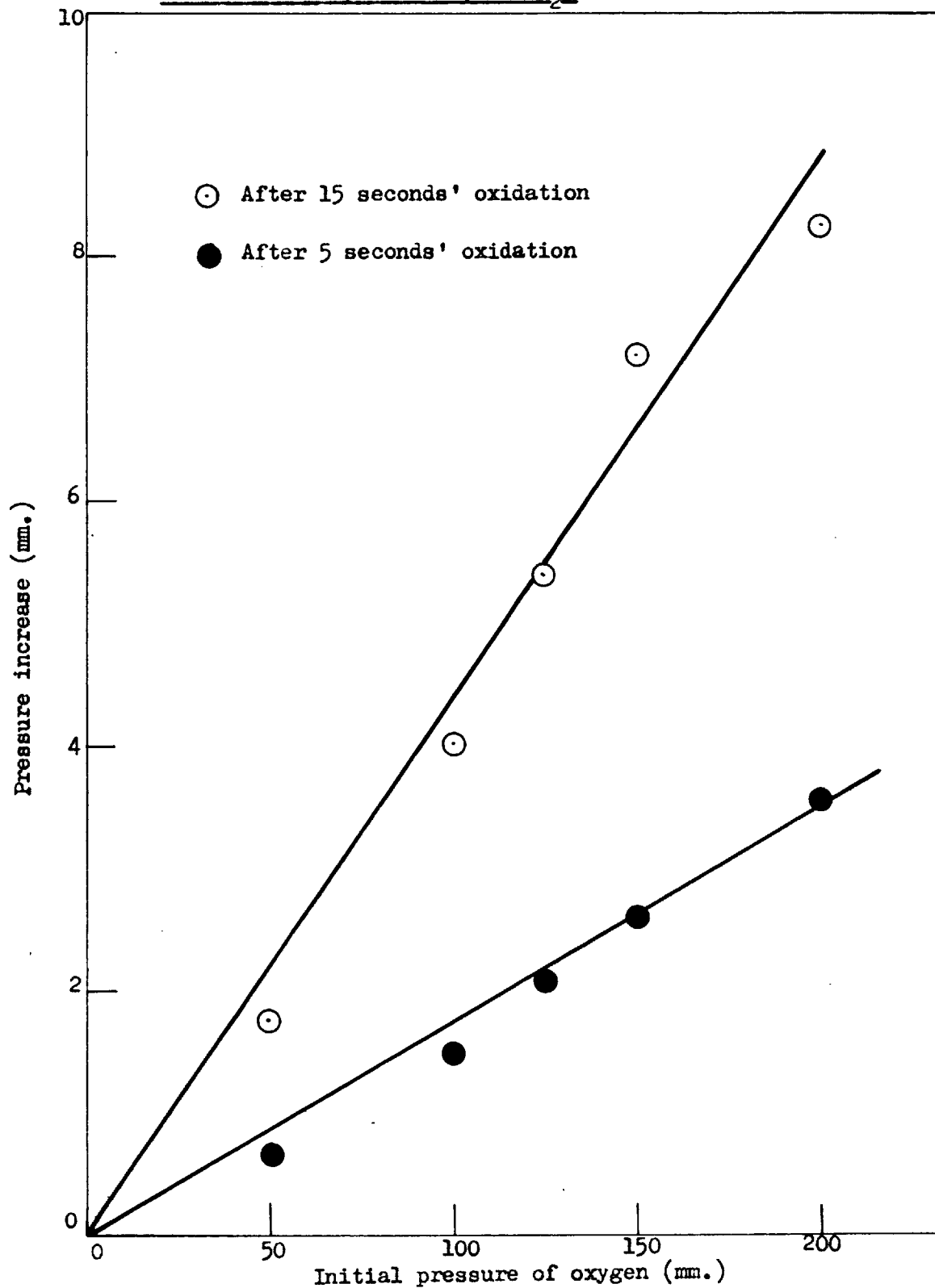


Figure 47

Influence of hydrogen bromide on the pressure change
accompanying the oxidation of polyethylene

Temperature: 430°C

Initial pressure of oxygen: 150 mm.

Sample weight: 6.4 mg. Initial total pressure (with N₂): 200 mm.

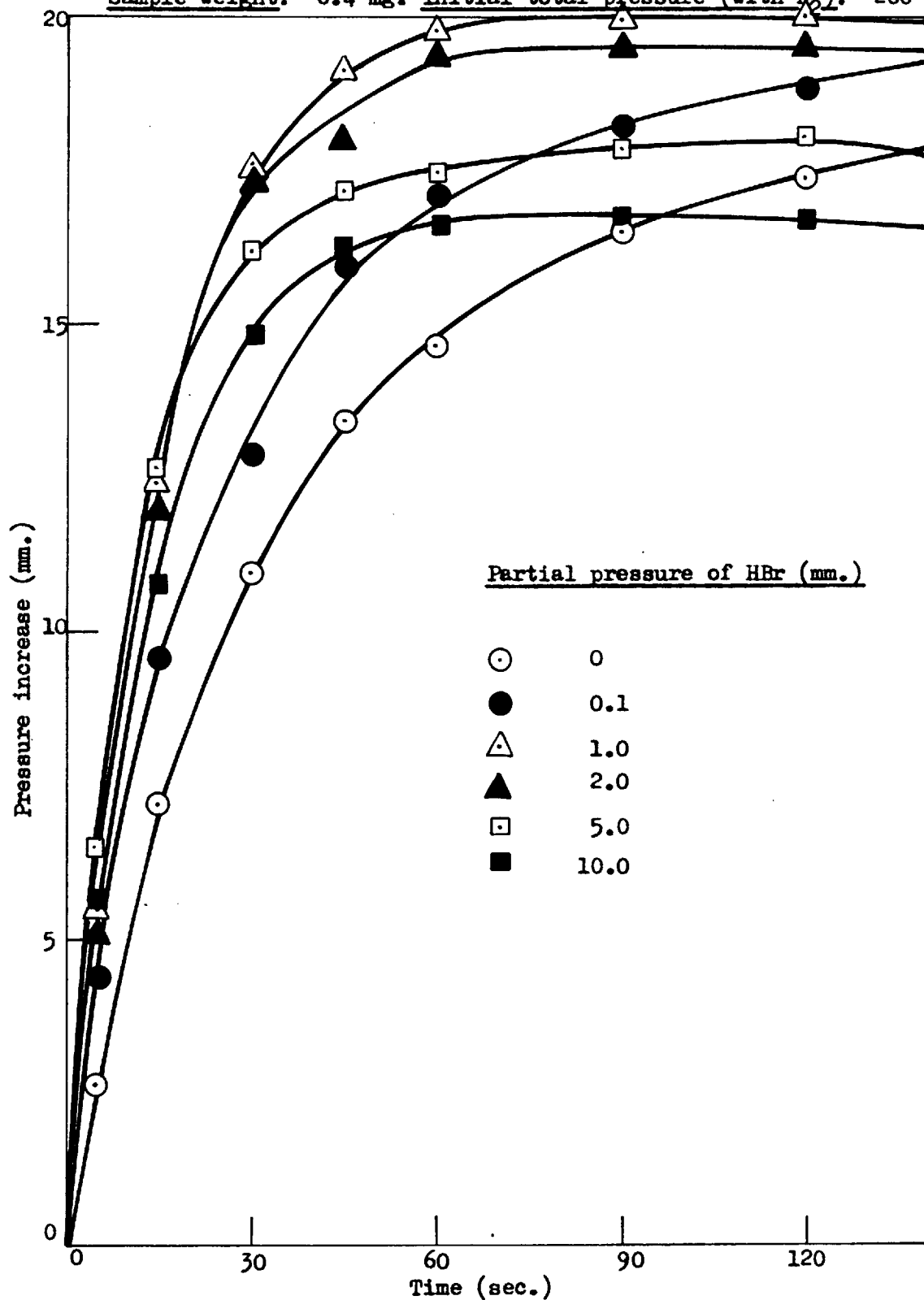


Figure 48

Influence of hydrogen bromide on the rate of pressure increase during the oxidation of polyethylene

Temperature: 430°C

Initial pressure of oxygen: 150 mm.

Sample weight: 6.4 mg.

Initial total pressure (with N_2): 200 mm.

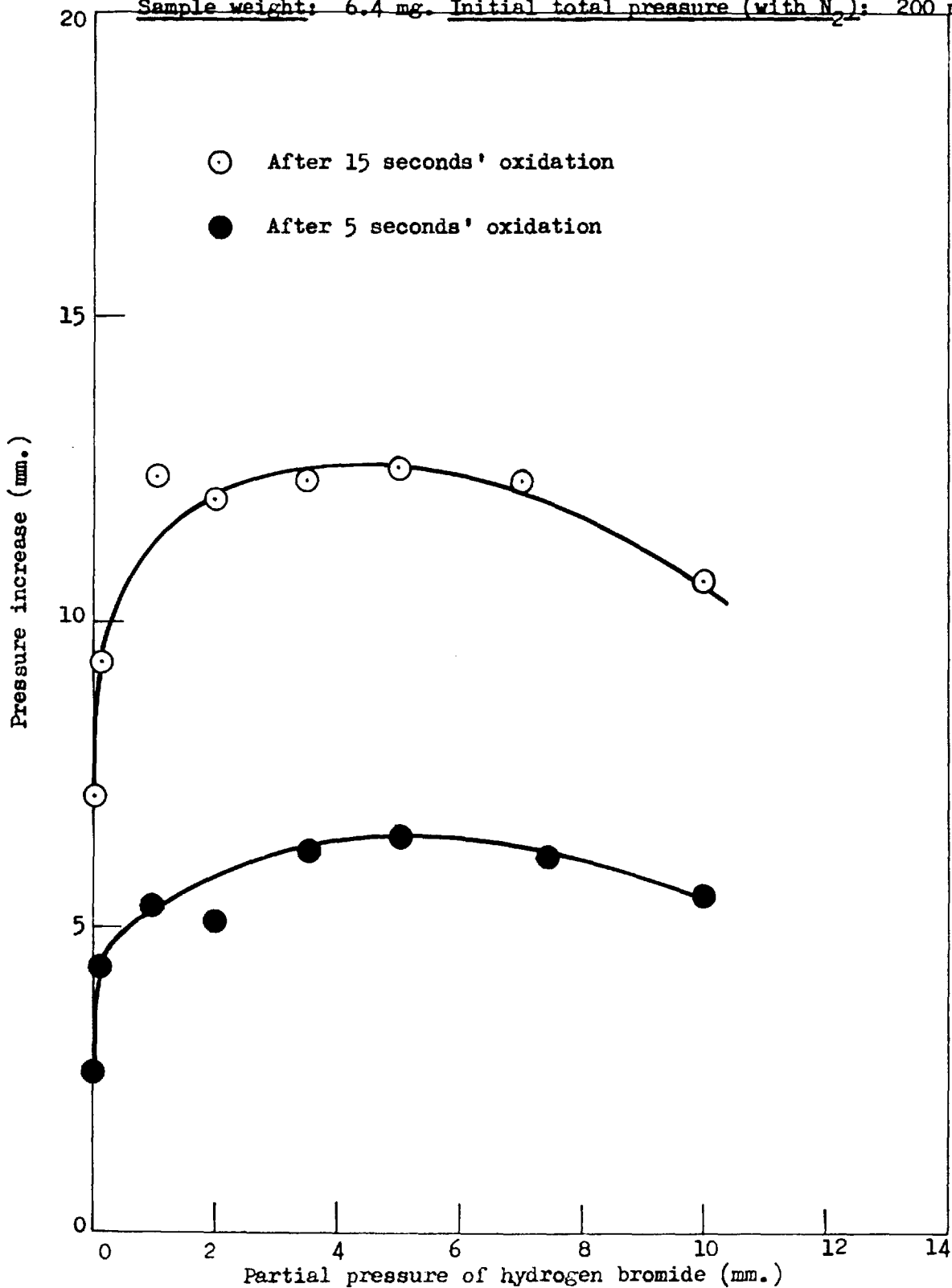


Table 25

Influence of the concentration of hydrogen bromide on the pressure change accompanying the oxidation of polyethylene

Temperature: 430°C Initial oxygen pressure: 150 mm.

Sample weight : 6.4 mg. Initial total pressure: 200mm. (with N₂)

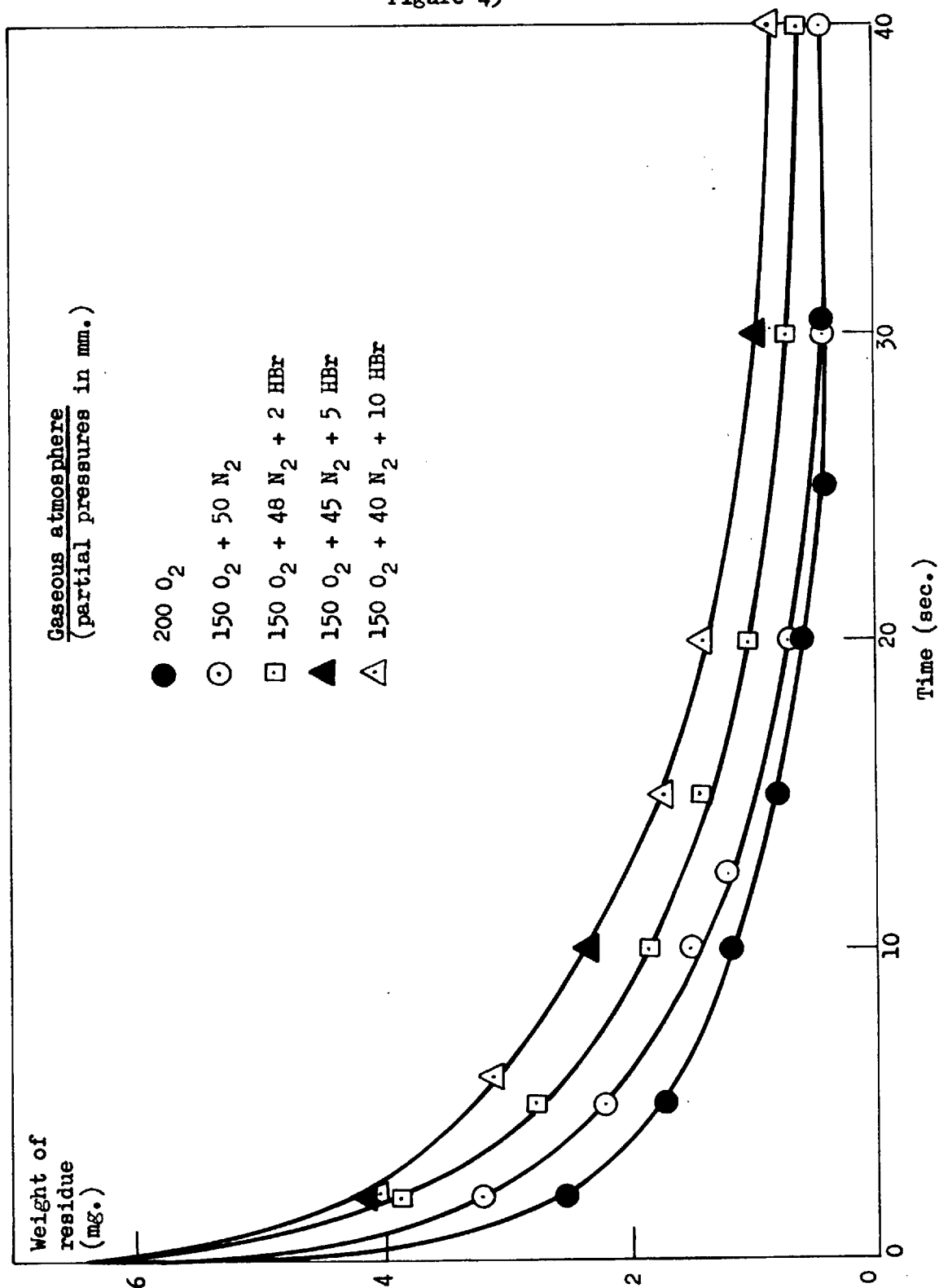
Partial pressure of HBr (mm.)	Maximum pressure increase (mm.)	Time of maximum (sec.)	Pressure increase after 300 sec. oxidation (mm.)
0	no subsequent decrease		19.8
0.1	no subsequent decrease		20.5
1.0	20.0	90	19.6
2.0	19.5	90	18.8
5.0	18.0	120	16.1
10.0	16.7	90	14.9

Runs were carried out with oxygen + hydrogen bromide mixtures in the absence of polymer. Small pressure decreases were observed. For example, the pressure decrease observed after 300 seconds' reaction of 5 mm. of hydrogen bromide with 150 mm. of oxygen was about 0.5 mm. In no case was the pressure decrease comparable with that observed during the oxidation of the polymer in the presence of an equivalent quantity of hydrogen bromide.

2. Loss of weight during oxidation and the influence of hydrogen bromide thereon

The loss of weight of the polymer was followed during oxidation in the presence and absence of hydrogen bromide. A constant sample weight and a constant total pressure, using nitrogen as the inert gas, were used throughout the series of runs. The weight of the residue is plotted as a function of time in figure 49. At a given time, the loss of weight of the sample was greater with 200 mm. of oxygen than with 150 mm. of oxygen. Hydrogen bromide reduced the loss of weight taking place after a given time compared with that found during oxidation in the absence of hydrogen bromide (table 26). The reduction in the loss of weight of the sample was greater using 5 and 10 mm. of hydrogen bromide than that observed using 2 mm. of this additive although there was no significant difference in the results obtained in the presence of the two higher concentrations of hydrogen bromide. The final residue weight after complete oxidation was the same for the two oxygen pressures used (table 26). The presence of hydrogen bromide, however, increased slightly the final residue weight.

Figure 49



Change in weight of polyethylene samples during oxidation
showing the influence of hydrogen bromide

Temperature: 430°C

Sample weight: 6.4 mg.

Table 26

Influence of hydrogen bromide on the loss of weight of polyethylene during oxidation

Temperature : 430°C

Sample weight : 6.4 mg.

Total pressure : 200 mm. (with nitrogen)

Gaseous atmosphere		Weight loss after 5 seconds (mg.)	Rate constant for intermediate stage (sec. ⁻¹)	Final residue weight (mg.)
O ₂ (mm)	HBr (mm)			
200	0	3.9	0.75	0.4
150	0	3.2	0.70	0.4
150	2	2.6	0.64	0.6
150	5	2.2	0.56	0.8
150	10	2.3	0.56	0.8

Plots of $\log_{10} r$ (where r is the residue weight in mg.) against time are given in figure 50. In all cases the plots are approximately linear in the intermediate stages of oxidation although the rate of loss of weight is greater in the initial stages and smaller in the final stages of oxidation. Thus, for all the conditions investigated, first-order rate constants could be obtained from the linear portions of these curves and the values obtained are given in table 26.

The rates of loss of weight in the intermediate stages of oxidation under the conditions investigated were not very different. The figures in table 26 do suggest, however, that hydrogen bromide reduces the rate of loss of weight of the polymer in the intermediate stages of oxidation.

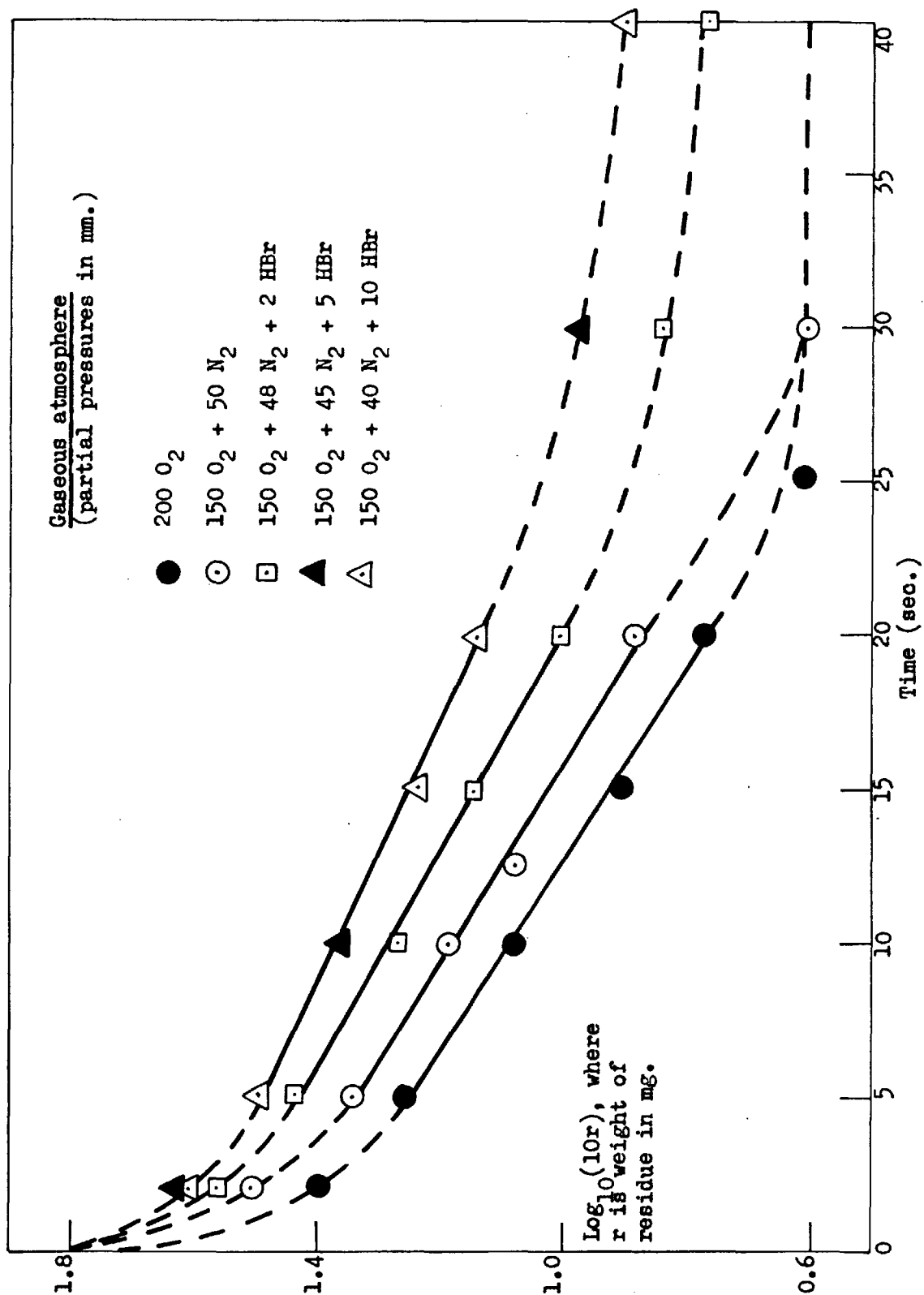
It was observed during these investigations that, as the extent of oxidation increased, the residue withdrawn from the reaction vessel became progressively darker in colour (the final residue was black). It was also observed that, throughout the oxidation, the solidified residue formed a fairly even layer on the bottom of the silica boat.

3. Formation of volatile products

(a) Nature of the products and their rate of formation

The formation of volatile products during the oxidation of polyethylene was studied using a constant sample weight and a constant initial oxygen concentration. The samples of volatile products obtained after varying oxidation times were analysed for both hydrocarbons and oxygenates. The production of all the hydrocarbons followed a similar pattern to that shown by the results for but-1-ene given in figure 51. The concentration of hydrocarbons rose sharply to a maximum at about 30

Figure 50



'First-order' plots of loss of weight results from the oxidation of polyethylene

Temperature: 430°C

Sample weight: 6.4 mg.

Figure 51

Formation of but-1-ene during the oxidation of polyethylene showing the influence of hydrogen bromide

Temperature: 430°C

Sample weight: 6.4 mg.

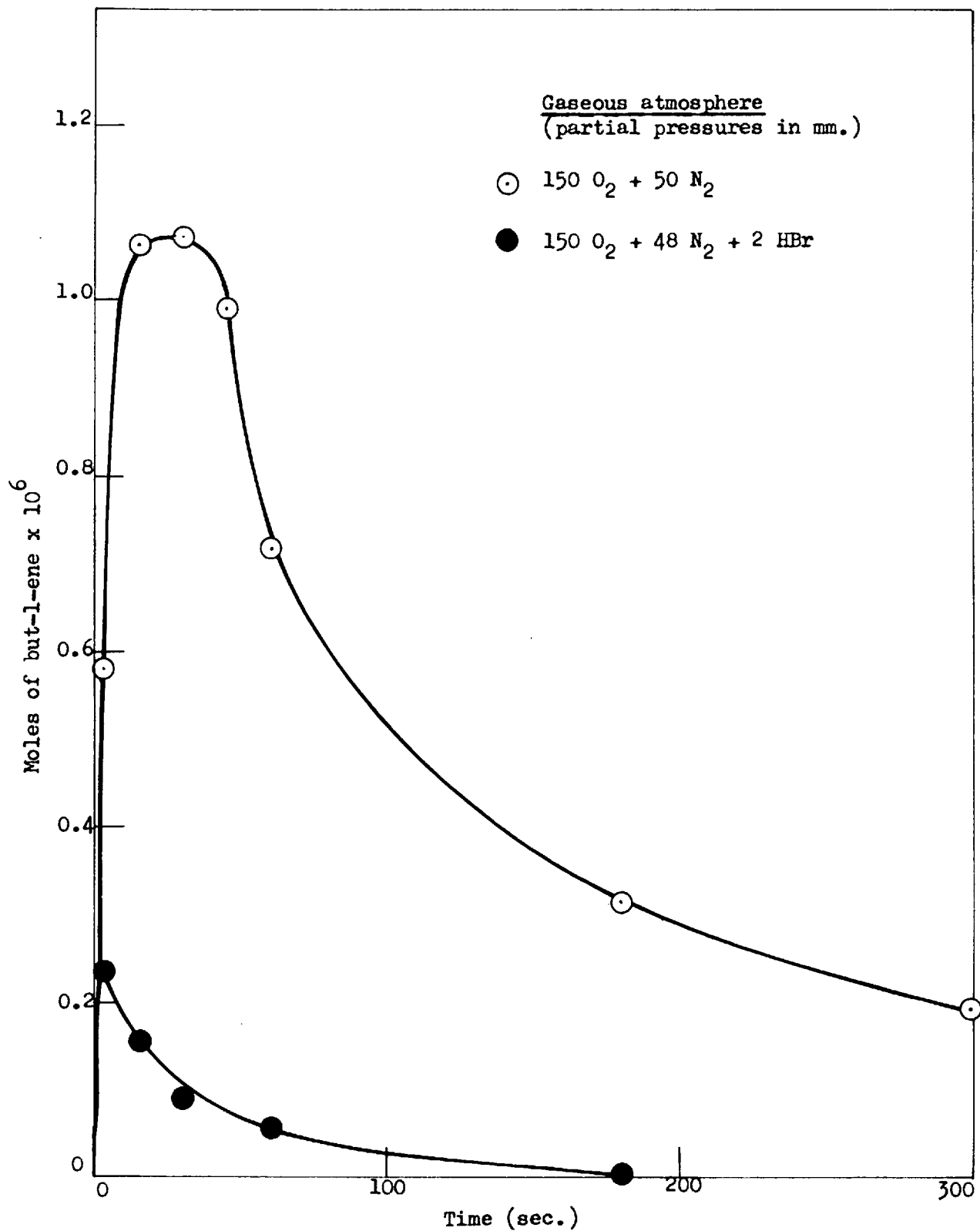


Table 27

Volatile hydrocarbon products formed by the oxidation of polyethylene and the quantities of such products formed where this was measured

Temperature : 430°C

Sample weight : 6.4 mg.

Initial oxygen pressure : 150 mm.

Total initial pressure, (O₂+N₂) : 200 mm.

Hydrocarbon	Yield after 30 seconds' oxidation		Yield after 300 seconds' oxidation
	(moles x 10 ⁸)	(weight per cent of polymer weight loss)	(moles x 10 ⁸)
Propane	40	0.29	35
Propene	451	2.9	182
Butane	20	0.19	4
But-1-ene	107	1.0	19
But-2-ene (trans)	trace	-	-
But-2-ene (cis)	trace	-	-
Pentane	trace	-	-
Pent-1-ene	26	0.31	-
Pent-2-ene (trans)	trace	-	-
Pent-2-ene (cis)	trace	-	-
Hexane	trace	-	-
Hex-1-ene	trace	-	-

seconds' oxidation after which time the concentration gradually fell. A list of hydrocarbon products identified is given in table 27 together with the quantities present after 30 seconds' and 300 seconds' oxidation for those products where a quantitative estimate was possible. On the chromatographic column used the carbon monoxide peak coincided with that due to ethane + ethylene so that no quantitative estimation of these two hydrocarbons was possible. Also given in table 27 is the quantity of a given product present after 30 seconds' oxidation expressed as a percentage of the weight of polymer lost after 30 seconds' oxidation. These figures may be compared with similar measurements of product formation obtained from experiments on the purely thermal degradation of polyethylene (table 21). The comparison shows that whereas for the alkanes these quantities are of a similar order for both oxidation and pyrolysis, for the alkenes the quantities obtained from oxidation experiments are greater than those obtained from pyrolysis experiments.

In figure 52, for some of the hydrocarbon products, the quantity of product formed after a given time is plotted against the loss of weight of the polymer which had occurred after that time. For the alkanes the amounts formed were approximately proportional to the loss of weight of the sample. For the alkenes, however, the quantities of product formed per mg. of polymer weight lost appeared to increase as oxidation continued.

A list of the volatile oxygenates which were identified are given in table 28 together with the quantity of each product formed after 30 seconds' and after 300 seconds' oxidation. Of these only

Formation of hydrocarbons as a function of the loss of weight of polyethylene during oxidation

Temperature: 430°C Initial oxygen pressure: 150 mm.

Sample weight: 6.4 mg. Initial total pressure (with N₂): 200 mm.

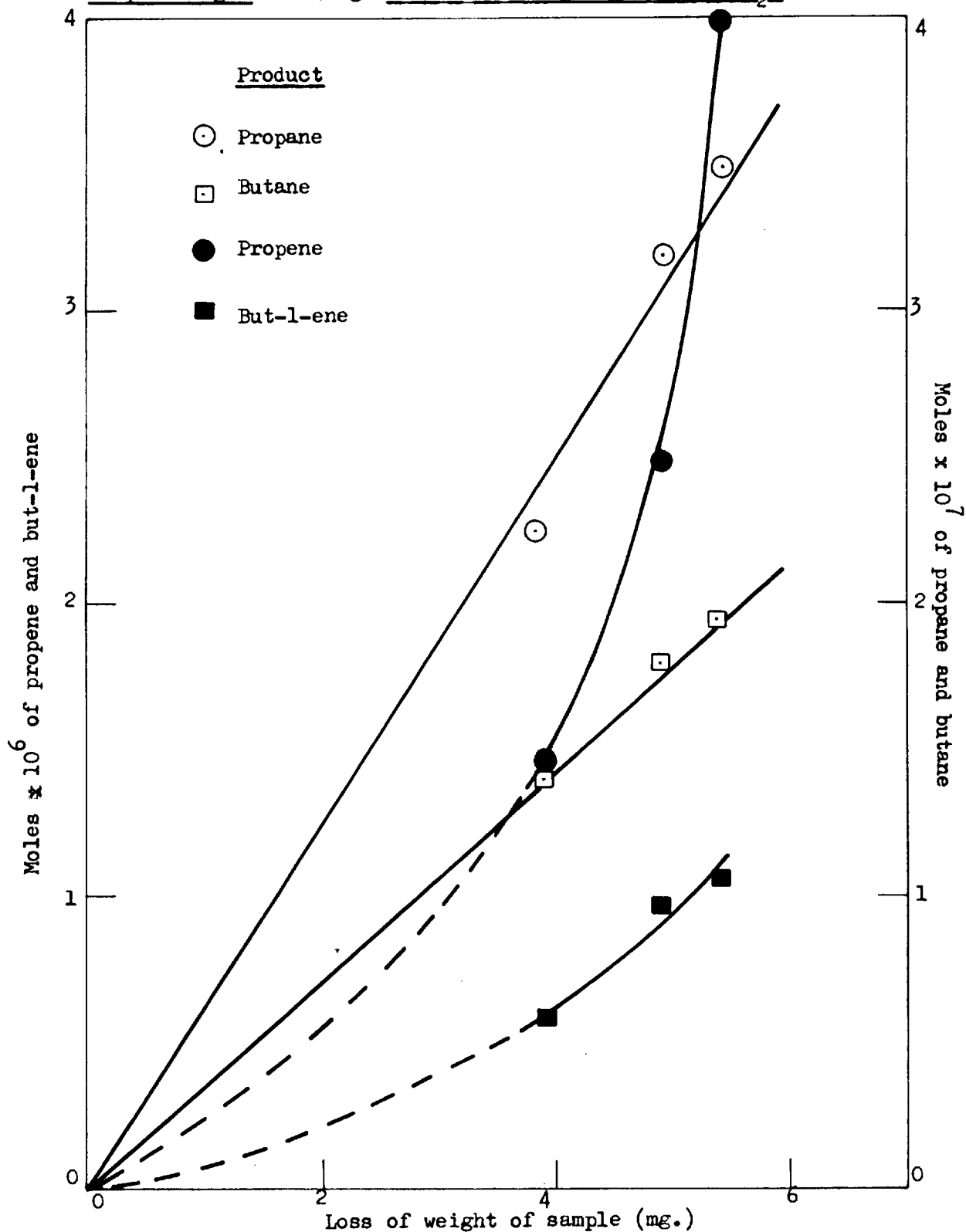


Table 28

The volatile oxygenated products formed by the oxidation of polyethylene

Temperature : 430°C Sample weight : 6.4 mg.

Initial oxygen pressure : 150 mm.

Initial total pressure, (O₂+N₂) : 200 mm.

Product	Quantity present (moles x 10 ⁶)	
	After 30 seconds' oxidation	After 300 seconds' oxidation
Carbon monoxide	-	339 *
Water	-	409 *
Carbon dioxide	24.5	71
Acetone	0.42	0.82
Propanal	0.73	0.54
Butanone	0.21	0.28

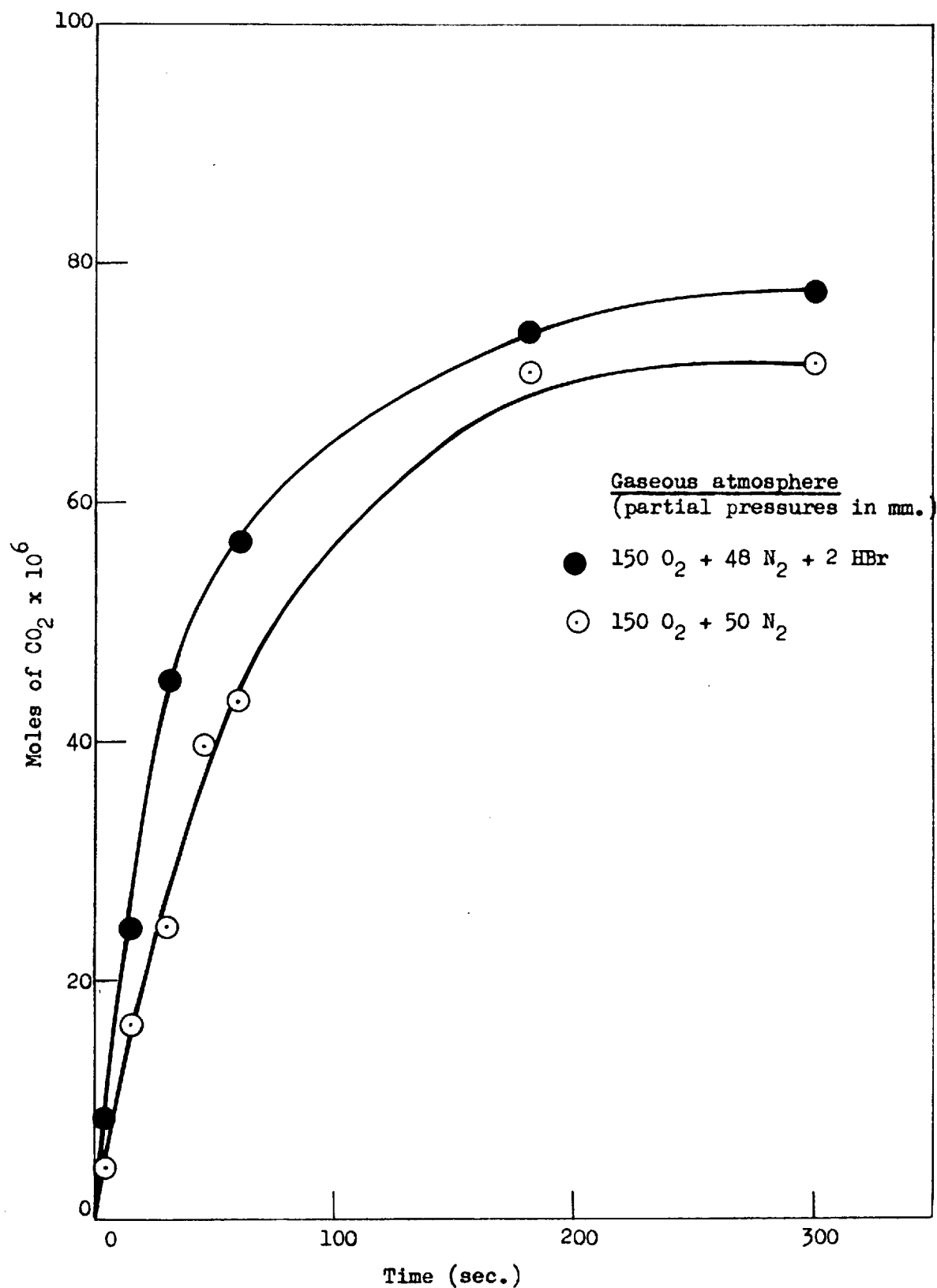
* estimated as described on page 185.

Figure 53

Formation of carbon dioxide during the oxidation of polyethylene showing the influence of hydrogen bromide

Temperature: 430°C

Sample weight: 6.4 mg.

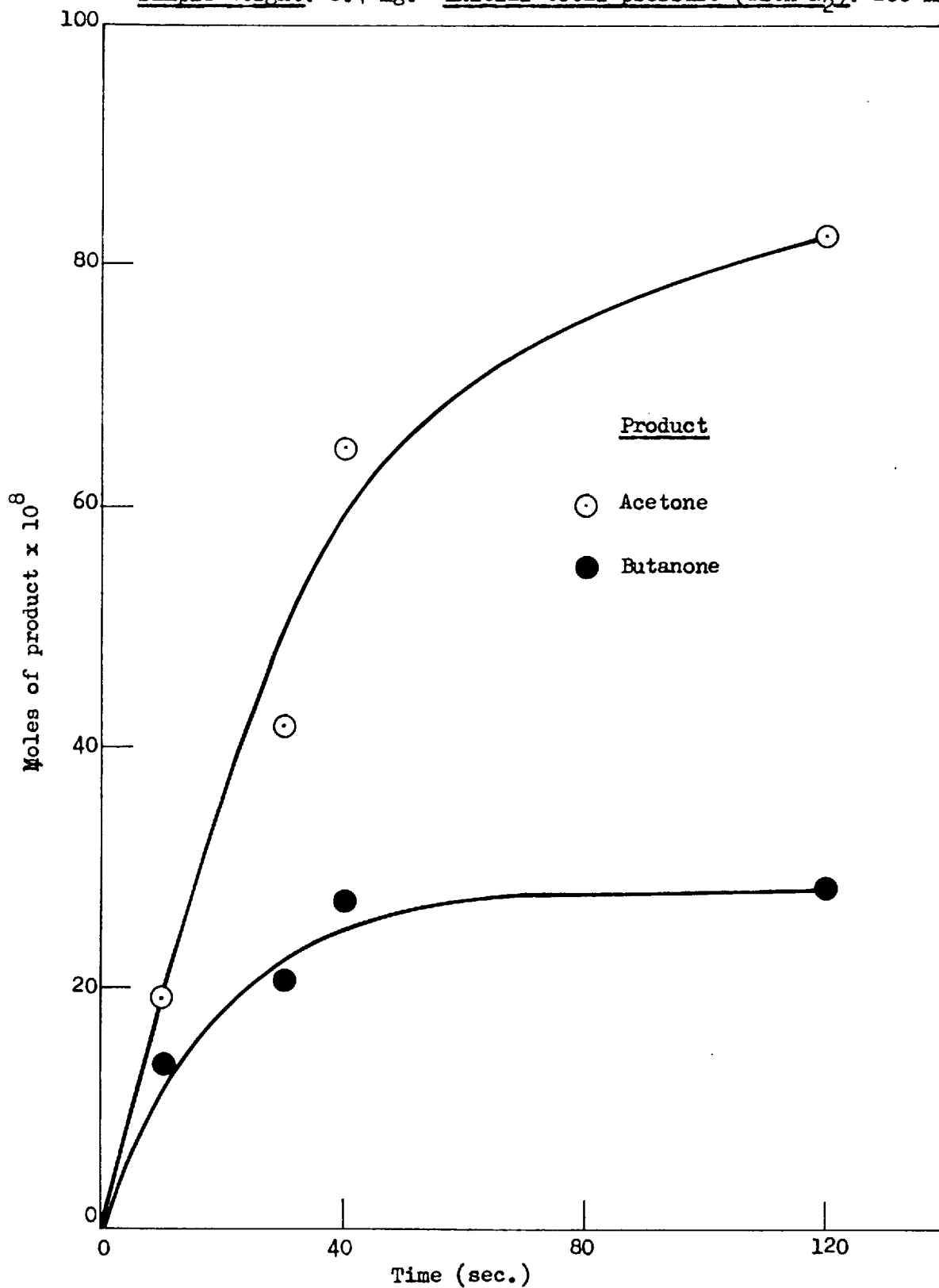


Formation of acetone and butanone during the oxidation of polyethylene

Temperature: 430°C

Initial oxygen pressure: 150 mm.

Sample weight: 6.4 mg. Initial total pressure (with N₂): 200 mm.



propanal showed a maximum concentration at about 30 seconds with a subsequent decay as oxidation continued. The formation of carbon dioxide is shown in figure 53 and that of acetone and butanone is given in figure 54.

Three products of oxidation detected by gas-chromatographic analysis (using column 2) were not positively identified; the peak areas of these products were comparable with those of the oxygenated products which were identified. The retention times of these unidentified products did not correspond to those of any of the simpler alcohols or carbonyl compounds. It is thought probable, therefore, that these products were epoxyalkanes.

The oxygen uptake was measured in experiments carried out under conditions similar to those described above and the results are shown in figure 55. The pressure increase accompanying oxidation under these conditions is plotted against the oxygen uptake in figure 56. The pressure increase, at a given time, was approximately proportional to the quantity of oxygen consumed.

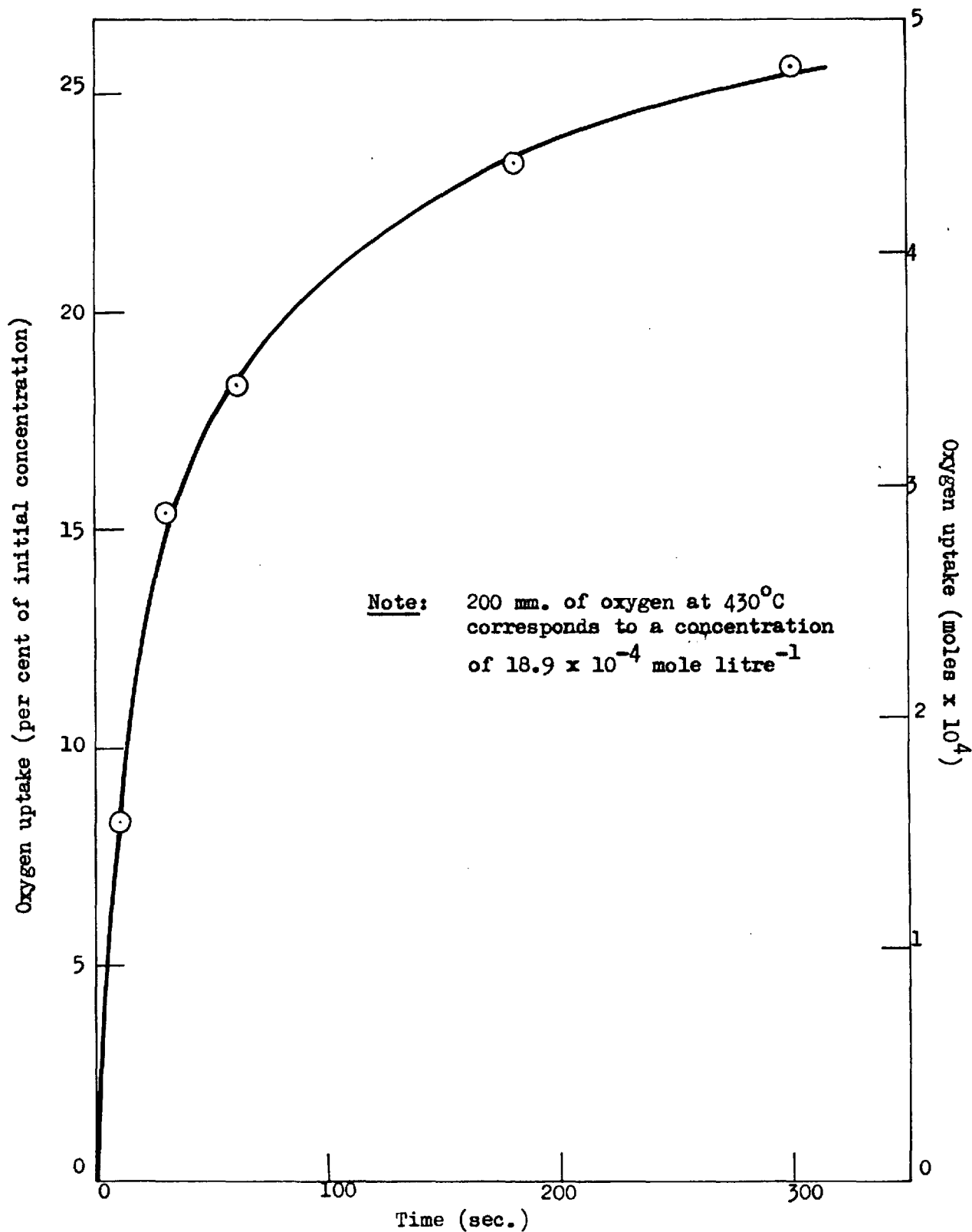
No estimation was made of the quantities of water and carbon monoxide formed during oxidation so that a direct reactant-product balance is not possible. It may be assumed, however, that the quantities of ethane and ethylene, which were not determined, are of the same order as those of the other hydrocarbons. If it is also assumed that all the carbon not present in those products quantitatively determined is present in carbon monoxide, then the quantity of carbon monoxide formed may be estimated. By means of similar assumptions with respect to hydrogen, the quantity of water formed may be estimated. Such estimations

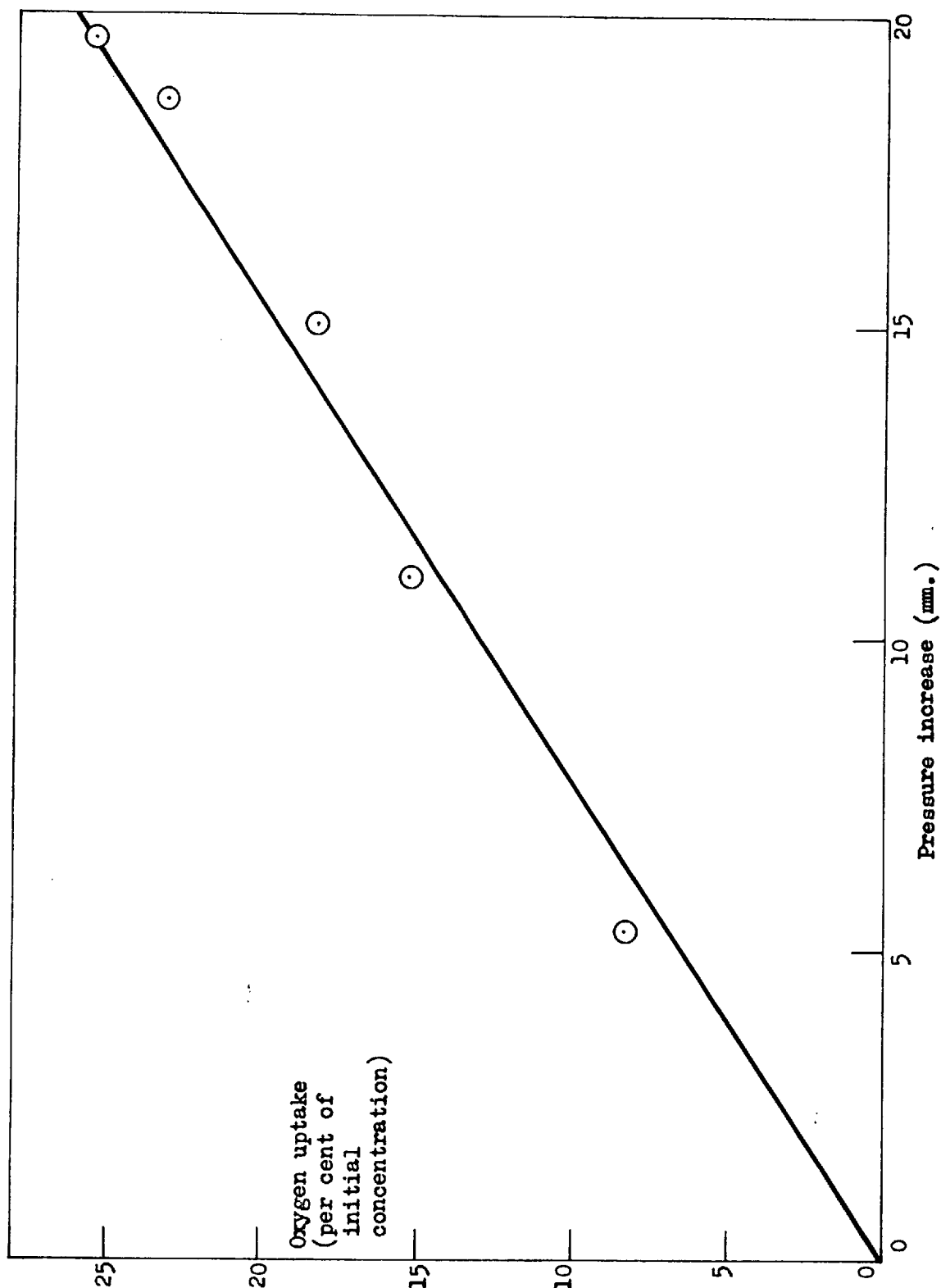
Figure 55

Oxygen uptake accompanying the oxidation of polyethylene

Temperature: 430°C Initial oxygen pressure: 150 mm.

Sample weight: 6.4 mg. Initial total pressure (with N₂): 200 mm.





Pressure increase accompanying the oxidation of polyethylene
as a function of oxygen uptake

Temperature: 430°C Initial oxygen pressure: 150 mm.

Sample weight: 6.4 mg. Initial total pressure (with N₂): 200 mm.

are liable to be valid only for the later stages of the oxidation reaction where the quantities of hydrocarbons other than those detected are likely to be negligible. The quantities of carbon monoxide and water formed after 300 seconds' oxidation of the polymer were estimated in this manner and are given in table 28. It was assumed in the calculation that the products corresponded to the oxidation of 6 mg. of polyethylene, the loss of weight which was observed in this time. The validity of these calculations was checked in the following way. If it is assumed that the total product spectrum for 300 seconds' oxidation is given by the appropriate columns in tables 27 and 28, the increase in the total number of moles in the system corresponding to 300 seconds' oxidation may be calculated. From the calibration of the reaction vessel system with the standard volume vessel the pressure increase corresponding to the increase in the total number of moles may also be calculated. The value obtained is compared with the experimental value shown in table 29. Furthermore, from the quantities of the oxygenated products given in table 28, the oxygen uptake may be calculated and the value obtained can be compared with that determined experimentally in table 29. The agreement between the observed and calculated pressure increase and oxygen uptake suggests that the estimated quantities of water and carbon monoxide given in table 28 are reasonable.

(b) Influence of initial oxygen concentration

The hydrocarbon products present after 300 seconds' oxidation were analysed in a series of experiments in which the concentration of oxygen initially present was varied. The results for three of the products are given in figure 57. The quantity of a given hydrocarbon present increased as the initial concentration of oxygen was reduced.

Table 29

The pressure increase and oxygen uptake accompanying the oxidation of polyethylene

Temperature : 430°C Sample weight : 6.4 mg.

Initial oxygen pressure : 150 mm.

Initial total pressure, (O₂+N₂) : 200 mm.

Time of oxidation : 300 seconds

Property	Value estimated from product analysis	Experimentally determined value
Pressure increase (mm.)	19.6	19.8
Oxygen uptake (moles x 10 ⁴)	4.85	4.45

Figure 57

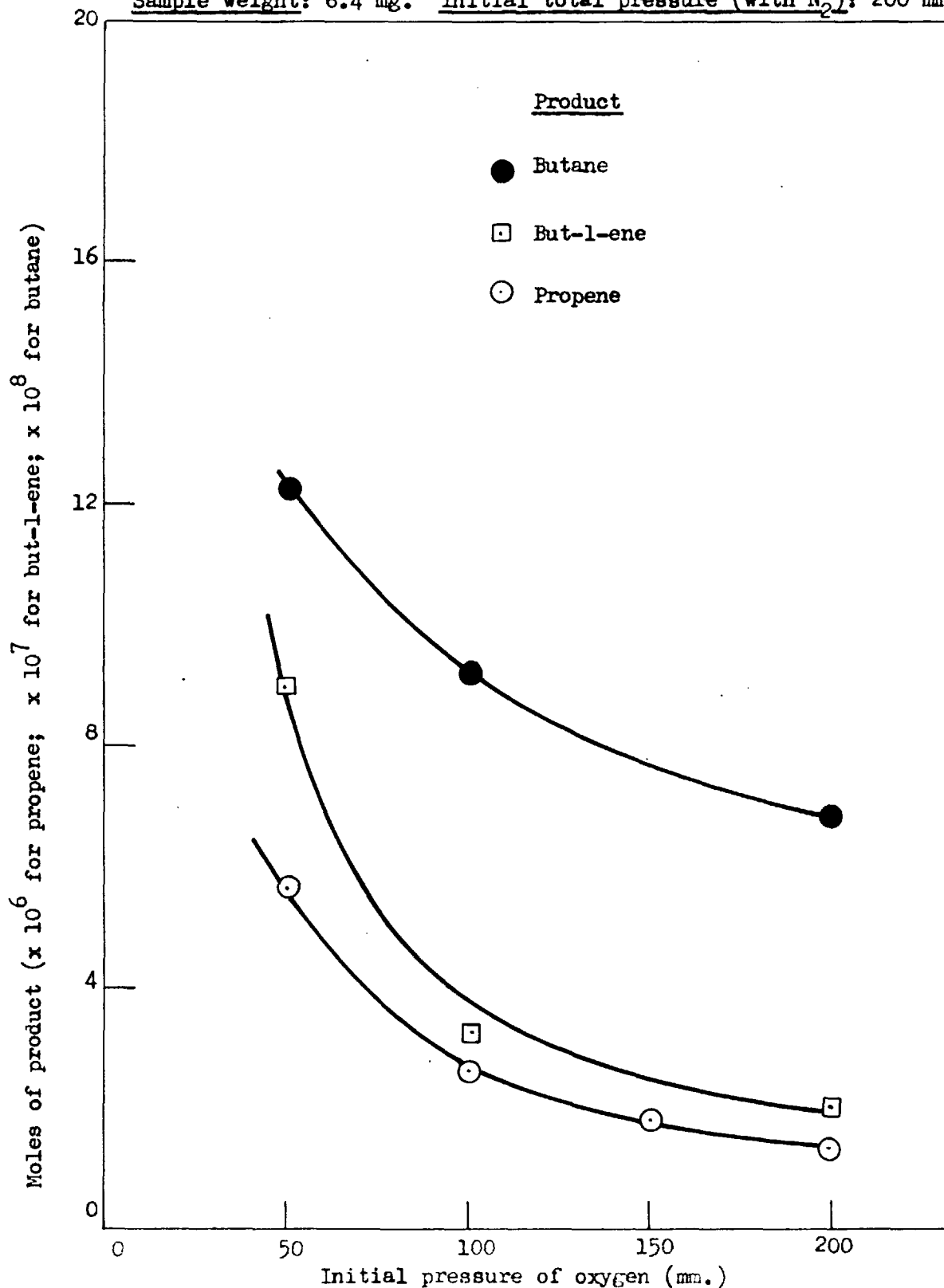
Influence of initial oxygen pressure on the formation of hydrocarbon products during the oxidation of polyethylene

Temperature: 430°C

Time of oxidation: 300 seconds

Sample weight: 6.4 mg.

Initial total pressure (with N₂): 200 mm.



(c) Influence of hydrogen bromide

The formation of volatile products during the oxidation of polyethylene in the presence of hydrogen bromide was studied. The results for but-1-ene, which were found to give a pattern of behaviour similar to that found for all the hydrocarbon products, are given in figure 51. The maximum concentration was substantially less than that observed during the oxidation of polyethylene in the absence of the additive. The maximum occurred within the first few seconds of the oxidation reaction and thereafter the concentration of the hydrocarbon decreased.

The formation of carbon dioxide during oxidation in the presence of hydrogen bromide is shown in figure 53. The rate of formation of this product was greater than that observed during oxidation in the absence of hydrogen bromide. The formation of other oxygenated intermediate products was not studied.

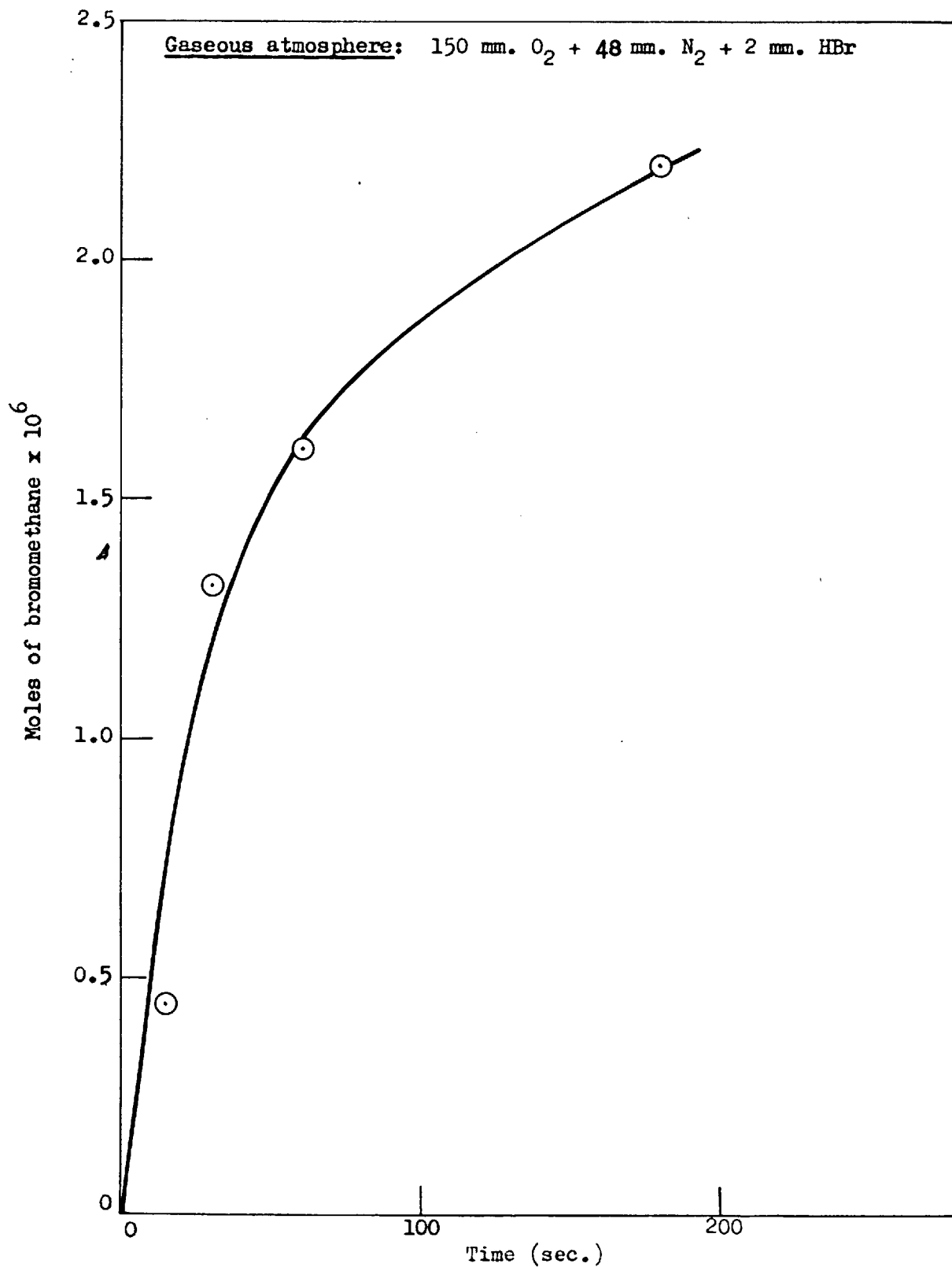
Bromomethane was found to be a product of the oxidation of polyethylene in the presence of hydrogen bromide and its formation is shown in figure 58. The quantity of this product increased throughout the stage of oxidation studied. No other organic bromides were found among the oxidation products.

Figure 58

Formation of bromomethane during the oxidation of polyethylene
in the presence of hydrogen bromide

Temperature: 430°C

Sample weight: 6.4 mg.



DISCUSSIONCONTENTS

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A The significance of the different types of experimental measurement

The aim of the present work was to investigate the influence of certain additives on the thermal and oxidative degradation of polyethylene. It is useful, at this juncture, to consider the context in which these studies were made. It was hoped that the results obtained would make possible a fuller understanding of the mechanism by which certain bromine-containing additives inhibit the burning of alkenic polymers. The measurements made in this work involved the degradation of polyethylene at sub-flame temperatures and are therefore relevant to the rate at which a combustible fuel mixture is supplied to the flame of a burning polymer. Thus, in terms of the flammability of polymers, the rate of pyrolysis may be defined as the rate at which combustible products are supplied to the flame. The relation between the rate of pyrolysis defined in this way and the results obtained from each of the methods of measurement used in this work will now be discussed.

For polyethylene, where chain scission is thought to be a completely random process, the rate of degradation may be obtained by the measurement of either the rate of chain scission or the rate of loss of weight of the polymer, provided that the loss of volatile molecules from the sample is not controlled by their rate of evaporation. Thus the weight loss measurements, in conjunction with chemical analysis of the residue, provide the most direct measurement of the rate of pyrolysis of the polymer.

Pressure measurements may, at best, be used only for a comparative study of the rate of degradation of the polymer. It must

be noted that molecules of different size evaporate from the molten polymer and whereas two molecules of different size make the same contribution to the increase in pressure, their contribution to the weight loss will differ. If, however, for a reaction which involves random chain scission, the pressure increase due to the evaporation of the primary degradation products could be directly determined, pressure measurements would give a reliable indication of the relative rates of degradation of the polymer in different atmospheres. In practice, a static system must be used to determine pressure change so that the value of such measurements depends on the extent to which the products are prone to further pyrolysis in the gas phase and condense in the cooler parts of the reaction vessel system. If, as in this work, a gaseous additive influences the rate of degradation of products in the gas phase, pressure measurements alone cannot give a reliable indication of the relative rates of degradation of the polymer sample. Used in conjunction with other measurements, however, pressure measurements facilitate comparison of reactions which occur in the gas phase with those which take place within the polymer itself.

Product analysis is of limited usefulness since, with the techniques employed, it was possible to determine only the rate of production of C_1 - C_7 hydrocarbons which constitute a small proportion of the total products. With this limitation, product analysis provided useful information of a qualitative nature for both the thermal and oxidative degradation reactions. The quantitative use of the data obtained was limited by the extent to which further degradation of the primary products of degradation of the polymer occurred in the gas phase.

This discussion leads to the conclusion, therefore, that loss of weight determinations provide the most direct and reliable measurement of the rate of degradation of the polymer. Moreover, since it was observed that, for the thermal degradation of the polymer in a number of gaseous atmospheres, the rate of loss of weight was proportional to the weight of the residue (figures 16,19,20,24-27, table 14), the influence of additives on the reaction may be discussed directly in terms of first-order rate constants. Measurements of pressure change and analysis of products, although by themselves of less significance, do, nevertheless, provide useful information from which deductions can be made regarding the mechanisms of the reactions concerned.

Since the results from loss of weight measurements are used frequently in this Discussion, it is instructive to compare these results with those obtained in previous work. This comparison is limited to the few cases in which the experimental conditions used in this work correspond to conditions used by other workers. The observation that, in the later stages of the thermal degradation reaction, the rate of loss of weight of polyethylene, in vacuo, is proportional to the weight of the residue (figure 16) is consistent with the results from some of the previous work (7,8). A comparison of rate constants for the thermal degradation of polyethylene is made in table 30; the agreement between the results of this and previous work is fair. Finally, it is noted that the value obtained for the activation energy for the pyrolysis of polyethylene in nitrogen (table 16) is close to the values obtained, for a variety of polyethylenes and experimental conditions, by previous workers (table 2). Thus, insofar as a

Table 30

Rate constants for the loss of weight of polyethylene during thermal degradation; the results of the present work compared with previously published results

Experimental conditions		Source of data	Rate constant (min. ⁻¹)
Gaseous atmosphere	Temperature (°C)		
Vacuum	430	Present work (table 13)	8.7×10^{-2}
Vacuum	430	Extrapolated from the results given in reference 7 (also given in tables 1 and 2)	9.9×10^{-2}
200 mm. N ₂	400	Present work (table 16)	5.6×10^{-3}
Vacuum	392	Reference 7	7.5×10^{-3}

comparison is possible, the kinetic data obtained in the present work agree satisfactorily with the data obtained previously.

B The influence of different volatile bromine compounds on the thermal degradation of polyethylene

The most fundamental observation was that at both 400 and 430°C relatively small amounts of hydrogen bromide (10-40 mm.) reduced the rate of loss of weight of the polymer by up to 30-40 per cent (figures 22,23, table 16). Hydrogen bromide, therefore, retards, but does not inhibit, the pyrolysis of polyethylene. For a given pressure of hydrogen bromide in the system, the rate of loss of weight is not affected by changes in the total pressure (table 17). For a constant total pressure in the system, the retardation increases with the partial pressure of hydrogen bromide (figure 28).

The rate of loss of weight of the polymer is also reduced in atmospheres containing certain volatile organic bromides (figure 29, table 19). Before the influence of the different organic bromides is compared, however, it is instructive to consider the relative thermal stabilities of these compounds in the temperature range used in these experiments.

Bromomethane is reported as being thermally stable up to temperatures of about 470°C (119). Above this temperature decomposition occurs yielding mainly methane and hydrogen bromide (119). Bromoethane, 1-bromopropane and 2-bromopropane decompose appreciably above 400°C yielding hydrogen bromide and the corresponding alkene (120); this is consistent with results obtained in the present work (table 20). Bromoethane (121) and 1-bromopropane (122) appear to decompose by

radical reactions whereas with 2-bromopropane, molecular elimination of hydrogen bromide takes place (123). The relative rates of decomposition of the monobromoalkanes are compared in table 31. The figures given have been calculated from the appropriate rate expressions (121,122,123). It is important to notice that for 1-bromopropane, first-order rate constants have been given for specific initial pressures of the compound, since it is known that the rate constant depends on the initial pressure (122). In two cases, where references are given, the rate constants have been taken directly from published results. The figures given in table 31, taken together with the work published on bromomethane, indicate that the rate of thermal decomposition of the monobromoalkanes decreases in the order 2-bromopropane > 1-bromopropane > bromoethane > bromomethane. This agrees with the results obtained during this work (figure 33).

The thermal stabilities of the monobromoalkanes are found to bear a close relationship to their influence (table 19) on the thermal degradation of polyethylene at 430°C. Thus:

- (i) Bromomethane is the most thermally stable and has the least influence on the rate of loss of weight.
- (ii) 1-Bromopropane and 2-bromopropane decompose rapidly and extensively to propene and hydrogen bromide and retard the loss of weight of the polymer to approximately the same extent as an equivalent quantity of hydrogen bromide; propene, on its own, has no influence (table 15).
- (iii) Bromoethane decomposes to ethylene and hydrogen bromide at a rate comparable with the rate of volatilisation of the polymer

Table 31

A comparison of the thermal stabilities of some organic bromides

k_1 = rate constant (sec.^{-1}) for first order decomposition of
organic bromide

$t_{\frac{1}{2}}$ = time taken (min.) for the decomposition of half the original
bromide

Property compared	Temperature	Bromide		
		Bromoethane	1-Bromopropane*	2-Bromopropane
$k_1 \times 10^4$	360	0.43	2.1 (40 mm.) reference 122	11.2
$k_1 \times 10^3$	380	0.16	1.0 (300 mm.) reference 124	3.7
$k_1 \times 10^2$	430	0.30	2.0 (40 mm.)	5.1
$t_{\frac{1}{2}}$	430	4.0	0.6 (40 mm.)	0.2

* The initial pressures of bromide to which these figures apply are given in this column.

(figure 33). Thus, under conditions where the additive and polymer are introduced into the reaction vessel simultaneously, the concentration of hydrogen bromide in the atmosphere increases as pyrolysis proceeds. This increase in the concentration of hydrogen bromide is thought to be directly responsible for the increased retardation of the pyrolysis of the polymer which was observed in the later stages of the reaction (figure 30). This conclusion is confirmed by the observation that if the additive is allowed to decompose in the reaction vessel for some time before the polymer sample is introduced, the decomposition of the polymer is retarded throughout the reaction (figure 31).

The influence of 1,2-dibromoethane is consistent with this correlation inasmuch as this compound decomposes rapidly to give hydrogen bromide and its presence reduces the loss of weight of the polymer (figure 32).

The important conclusion may be drawn, therefore, that a volatile organic bromide will retard the pyrolysis of polyethylene only under conditions where it decomposes to yield hydrogen bromide. Thus hydrogen bromide is the chemical species responsible for the observed decrease in the rate of degradation of the polymer.

Before the effect of hydrogen bromide on the production of volatile products is discussed, the formation of such products will be considered in the light of the theory of random chain scission which is thought to apply to the degradation of polyethylene.

The nature and quantity of the low molecular weight fragments (C_2 - C_7) found in this work agree satisfactorily with the results obtained by other workers (table 32). In this work a larger yield of

Table 32

The quantity of low molecular weight hydrocarbons obtained from the pyrolysis of polyethylene. The present work compared with previously published results.

Fraction	Source	Atmosphere	Temperature	Weight per cent. of total volatiles
C ₂ -C ₇ (polyethylene)	Present work (table 24)	100mm N ₂	430	3.3
C ₂ -C ₇ (polyethylene)	Present work (table 24)	80mm N ₂ + 20mm HBr	430	5.9
C ₁ -C ₇ (polyethylene)	10	Vacuum	405 - 470	1.1 (average)
C ₁ -C ₈ (polymethylene)	15	Vacuum	500	5.9
C ₁ -C ₈ (polymethylene)	15	760mm He	500	17.1

these products was obtained than in comparable experiments in vacuo (10), but it is known that the yield of low molecular weight hydrocarbons is increased by the presence of an inert gas (15) (table 32).

If it is assumed that polyethylene is degraded by a process of random chain scission, each of the products, volatile at the temperature of pyrolysis, has the same probability of being formed. From the number of moles of volatile product associated with a given loss of weight of polymer (table 24) it is possible to deduce the average molecular weight of the volatile products. The value of this quantity appropriate to the pyrolysis of the polymer in nitrogen is given in table 33. Now if it is assumed that the products with one, two, three etc. carbon atoms are all present in equal concentration, the number of carbon atoms in the largest volatile product molecule may be calculated from the average molecular weight of the products (table 33). Thus, for pyrolysis of the polymer in nitrogen, if all the molecules from $C = 1$ to $C = 29$ are present in equal concentration, the mole per cent and weight per cent of the C_2-C_7 fraction may be predicted. The values thus calculated, given in table 33, should be compared with the values given in table 24 which were obtained by using the experimentally determined value of the C_2-C_7 fraction. The agreement is sufficiently good to suggest not only that the model of random chain scission is of some use in interpreting the experimental results but also that the value calculated for the chain length of the largest molecule volatile at the temperature of pyrolysis may be used in future discussion.

Table 33

Quantities of low molecular weight hydrocarbons predicted on the assumption that polyethylene degrades by a process of random chain scission.

Atmosphere	100 mm N ₂
Mean molecular weight of volatile products obtained by experiment	212
Hence number of carbon atoms in the largest product molecule	29
Predicted mole per cent of C ₂ -C ₇ hydrocarbons	20.6
Predicted weight per cent of C ₂ -C ₇ hydrocarbons	6.2

By comparison of the results of both pressure increase measurements (figure 41) and of analysis of the C_2-C_7 fraction (table 24) it is apparent that hydrogen bromide increases the number of moles of volatile product per mg. of polymer volatilised. If the quantities of the individual hydrocarbons present in the C_2-C_7 fraction are compared, it is seen that the products both in the presence and absence of hydrogen bromide are straight chain hydrocarbons and that hydrogen bromide causes no significant change in the proportion of alkenic groups present in the product molecules (tables 22,23). The main point of significance, apart from the general increase in the number of molecules formed, is that hydrogen bromide increases the yields of the alk-2-enes at the expense of the corresponding alk-1-enes (figures 39,40, table 22). This is almost certainly due in part to the hydrogen bromide-catalysed isomerisation of the alk-1-enes to alk-2-enes in the gas phase which is known to occur rapidly at the temperatures concerned (125). That this reaction occurs under the conditions used in these experiments is confirmed by the results of experiments in which the additive was allowed to react only with the volatile products of degradation (compare columns B and D in table 23).

The observation that hydrogen bromide decreases the rate of loss of weight of the polymer suggests that its influence in increasing the fragmentation of the volatile products is due to its reaction with the primary degradation products in the gas phase. An increased rate of degradation of the volatile products would account for both the increase in the proportion by weight of low molecular weight species in these products and the increase in the number of moles of volatile

products associated with a given loss of weight of the polymer (table 24). It was by analysis of the C_2 - C_7 fraction of products that this effect was investigated (table 23). The volatile products of pyrolysis underwent further degradation in the gas phase even in the absence of hydrogen bromide and the presence of this compound greatly increased the extent of degradation. The presence of hydrogen bromide increased the yield of the low molecular weight fraction obtained after pyrolysis, in the absence of the polymer, of the products of the degradation by a factor of 1.7 (compare columns B and D in table 23) whereas this additive increased the yield of the low molecular weight fraction obtained in the presence of the degrading polymer by a factor of 1.8 (compare columns A and C in table 23). Thus the extent of the hydrogen bromide-induced decomposition of the volatile products is of sufficient magnitude to account completely for the increased yield of the C_2 - C_7 fraction of products which was observed during pyrolysis of the polymer in the presence of hydrogen bromide.

C The physical and chemical effects of hydrogen bromide on the thermal degradation of polyethylene

The influence of hydrogen bromide in decreasing the rate of loss of weight of polyethylene during thermal degradation may be due to one, or a combination, of effects. Some of the more probable ways in which hydrogen bromide may cause a reduction in the rate of loss of weight are discussed, in turn, below.

1. The temperature of the polymer sample

The degradation of the polymer is endothermic and this, combined with the effect of the evaporation of volatile products from

the polymer, might reduce the temperature of the polymer sample to below that of the reaction vessel. If this were the case, the temperature of the sample and hence its rate of pyrolysis, could be influenced by any factor which reduced the rate at which heat is supplied to the polymer sample. The preliminary experiments showed that, with the reaction vessel at a given temperature, the rate at which heat was transferred to a cold body placed in it depended on the nature of the surrounding gas (figure 9). For pure gases in the reaction vessel, the rate of heat transference decreased in the order helium > nitrogen > hydrogen bromide which is consistent with the known values for the thermal conductivities of these gases (126). The rate of heat transfer, although influenced by the nature of the gas present, was not affected, for a given gas, by its pressure. This latter effect is well known. However, the rate at which heat was transferred to the sample boat when the reaction vessel contained a nitrogen-hydrogen bromide mixture did not differ appreciably from that observed with an equivalent pressure of pure nitrogen (figure 10). Thus, if the rate of heat transfer in the nitrogen-hydrogen bromide mixture is the same as that in pure nitrogen, it seems improbable that the reduction in the rate of pyrolysis by hydrogen bromide is caused by a reduction of the temperature of the polymer sample. Moreover, the temperature of the reaction vessel was quite rapidly attained by a sample 60 times heavier than that generally used (figure 11). It is unlikely, therefore, that, under the conditions used for the loss of weight experiments, the temperature of the degrading polymer was appreciably below that of the reaction vessel. The time taken for the sample to attain the temperature of the reaction vessel

increased, however, with sample size (figure 11). This latter effect probably accounts, in part, for the non-linear relationship between the per cent loss of weight, for a given pyrolysis time, and the initial sample weight (figure 14, table 10).

The experiments on heat transfer are relevant in one respect to the experiments on the rate of loss of weight of the polymer. Thus it was observed that, for a given pyrolysis time, the loss of weight was greater in helium than in nitrogen (figure 18) whereas the rates of loss of weight for the later stages of pyrolysis were identical in these two atmospheres (figure 21). Thus the effect of nitrogen, compared with helium, is to increase the time taken for the sample to attain the temperature of the reaction vessel but, once this temperature is attained, the rate at which the sample loses weight is the same as the rate in helium.

2. The influence of total pressure

An increase in the total pressure in the system may decrease the chain length of the largest hydrocarbon molecule which is volatile at the temperature of pyrolysis and hence reduce the rate of loss of weight. An increase in total pressure from 100 to 400 mm. was, however, found not to influence the rate of loss of weight of the polymer (figure 17). In none of the experiments on the influence of additives was the change in pressure (due either to the accumulation of products or to the decomposition of an additive) such that the total pressure exceeded 400 mm. Only under two conditions of pyrolysis in the absence of additive was the rate of loss of weight found to be greater than that in 100-400 mm. of nitrogen. In the first case the polymer was degraded

in a reaction vessel under conditions of continuous evacuation and in the second case the polymer was degraded in the presence of its degradation products but with the reaction vessel initially evacuated (figure 15, table 13). The rate of loss of weight was greater in the former case than in the latter but it is not possible to deduce the reason for this. It is not thought, however, that the effect just described has any relevance to the differing rates of pyrolysis observed in the presence or absence of additives. Thus, in all experiments on the influence of additives on the rate of loss of weight of the polymer, the products were allowed to remain in the reaction vessel during the reaction and the total pressure remained within the range for which the rate of loss of weight was found to be independent of changes in total pressure.

3. Combination between bromine and the polymer

Pyrolysis of polyethylene in a reaction vessel containing hydrogen bromide may cause chemical combination between bromine and the polymer. This would tend to increase the weight of the residue compared with the corresponding weight of the residue in the absence of the additive. In order to investigate this, samples of the residue obtained by pyrolysis of the polymer in hydrogen bromide for different pyrolysis times were chemically analysed. No bromine was detected and the weight of the residue, in each case, was found to correspond to the total weights of carbon and hydrogen present (table 18). Some recent experiments, in which the pyrolysis of brominated polyethylenes (containing 12 per cent by weight of bromine, chemically combined with the polymer) was investigated, are also relevant in this context (127).

The sample of brominated polymer was placed in the reaction vessel under vacuum, and withdrawn after two minutes. No bromine was detected in the sample thus obtained and all the bromine originally present appeared as hydrogen bromide.

The absence of bromine in the polymer is not unexpected since it is known that, at the temperatures concerned, the equilibrium position of the reaction: bromoalkane $\rightleftharpoons$ alkene + hydrogen bromide, lies well to the right for both primary and secondary bromoalkanes (122,123,124). This is also consistent with the observation made in this work that no brominated hydrocarbons are present in the volatile products formed in the presence of hydrogen bromide.

4. The chemical influence of hydrogen bromide

(a) Values of certain quantities used in the discussion

The values of some of the quantities used in the discussion are given here for convenience. In each case a note is made of the manner in which the value was obtained.

(i) Bond strengths (kcal mole⁻¹). The values referring to polyethylene are approximate. The data used have been taken from Cottrell (128) except in the case where another reference is given.

C-H (primary) in polymer molecules = 100 (the value for butane is 101).

C-H (secondary) in polymer molecules = 90 (the value for butane (129) is 92.8).

C-C in polymer molecules = 75 (the value for the bond between the second and third carbon atoms in butane is 78; the value is probably somewhat less than this for the bond between carbon atoms in a polymer molecule).

H-Br = 87.

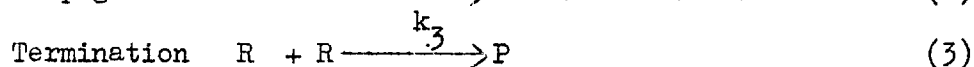
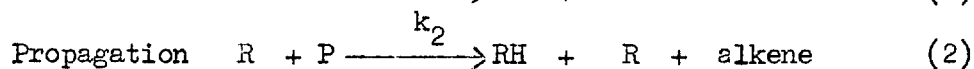
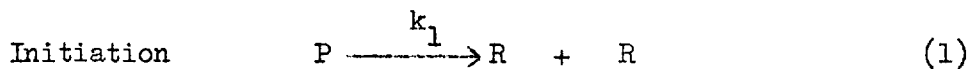
(ii) The concentration of secondary hydrogen atoms in the polymer phase, $[H_2^\circ] = 140 \text{ mole litre}^{-1}$. This has been calculated on the assumption that the density of the polymer sample is of the order of 1 gm. cm.^{-3}

(iii) The concentration of hydrogen bromide in the molten polymer at 430°C with 40 mm. of hydrogen bromide in the gas phase $= 10^{-3} \text{ mole litre}^{-1}$. The method used to estimate this quantity is described by Hildebrand and Scott (130). Some attempt was made in this calculation to account for non-ideal behaviour by using the solubility parameters for polyethylene (131) and hydrogen bromide (estimated in the manner described by Hildebrand and Scott (132)). The correction for non-ideal behaviour is not strictly applicable to solutions which involve polar molecules, such as those of hydrogen bromide, although it has been used successfully to interpret the data obtained from the investigation of some systems of this nature (for example, the solubility of water in hydrocarbons (133)). The assumptions made in the calculation of this quantity are such that the value obtained may be several orders of magnitude too large. The possibility of this degree of error is considered at that point in the discussion where the value of this quantity is used.

(b) The mechanism of the reaction in the absence of additives

Two alternative mechanisms have been proposed for the thermal degradation of polyethylene. One of these involves a molecular process and the other a free radical chain mechanism. Provided that none of

the possible physical effects of hydrogen bromide, described previously, is significant, however, the observation that hydrogen bromide decreases the rate of thermal degradation strongly suggests that the process involves, at least in part, radical chains. In the discussion of this reaction, therefore, it will be assumed that the breakdown of polyethylene, in the absence of additives which are effective at the relatively high temperatures involved (see p.108), occurs by the following series of reactions :



These reactions have been described in greater detail in section B.2(g) of the Introduction. The symbols P and R represent polymer molecules and primary alkyl radicals respectively and no distinction is made between molecules and radicals of different chain lengths. In reaction (2), hydrogen abstraction and chain scission occur simultaneously. The possibility of this reaction proceeding by two steps is discussed in Appendix 1. It is assumed that hydrogen abstraction, reaction (2), occurs predominantly by an intermolecular process. The results obtained in both the present investigation (which are discussed in this context on p.203) and in previous work (10) suggest that polyethylene degrades predominantly by a process of random chain scission so that the contribution of the intramolecular process to the degradation reaction is not thought to be significant.

Quantitative analysis of such a system is difficult and

inevitably certain simplifying assumptions must be made. Thus it is assumed that the rate of reaction of volatile radicals is greater than their rate of evaporation so that none of the reactions of type (2) leads to a termination step by the subsequent evaporation of the radical formed. Thus loss of weight occurs only as a result of the evaporation of a volatile alkene or of RH, the alkane produced by the subsequent reaction of the radical formed in reaction (2). Furthermore, it will be assumed that the concentration of radicals is small and that a steady state concentration is achieved. A unique feature of the system studied in this work is that the volume of the reaction phase decreases as the reaction continues and this effect must be taken into account in a calculation of the steady state concentration of radicals. The influence of volume change on the radical concentration is discussed in Appendix 2 and the conclusion is reached that it is possible, in the present instance, that this effect may be insignificant compared with the rate of formation and removal of radicals by chemical reactions. The influence of volume change is, therefore, neglected in the following discussion. It is also assumed that structural irregularities in the polyethylene chain, although they may influence the reaction in the initial stages, do not influence the later stages of the reaction which were investigated in this work.

The radical concentration (mole litre⁻¹) and the rate of bond scission, r_b (mole litre⁻¹sec.⁻¹), are given by the following equations:

$$[R] = (k_1[P]/k_3)^{\frac{1}{2}} \quad (a)$$

$$r_b = k_2[H\ 2^\circ][R] \quad (b)$$

$$\text{i.e.,} \quad r_b = k_2 [H_2^O] (k_1 [P] / k_3)^{\frac{1}{2}} \quad (c)$$

where $[H_2^O]$ represents the concentration of secondary hydrogen in the polymer phase. If it is also assumed that, at a given instant, the average chain length of the polymer molecules is m , for a process of random chain scission the fraction of scissions which lead to loss of weight is $2p/m$ (where for molecules of chain length greater than p , the probability of further reaction is greater than the probability of evaporation). The average molecular weight of molecules which evaporate is therefore $4p/2 = 7p$. The loss of weight will also be proportional to the volume of the sample which is given by w/d litres, where w gm. is the weight of the sample and d gm. litre⁻¹ is the density of the molten polymer. In addition it should be noted that $[P] = [H_2^O]/2m$. From equation (c), the rate of loss of weight (gm. sec.⁻¹) is given by:

$$r_w = 7(2)^{\frac{1}{2}} \cdot k_2 (k_1/k_3)^{\frac{1}{2}} \cdot [H_2^O]^{3/2} \cdot (p^2/d) \cdot w \cdot (1/m)^{3/2} \quad (d).$$

Since each of the terms in this equation (except w and m) is constant, the rate of loss of weight is given by:

$$r_w = K \cdot w \cdot (1/m)^{3/2} \quad (e)$$

where K is a constant. This equation predicts that the rate of loss of weight, for a polymer of given chain length, is proportional to the weight of the sample, which was found to be approximately the case for the pyrolysis of the polymer in vacuum (figure 16) and in inert gas atmospheres (figures 19,24-27). If, however, the average chain length of the polymer residue decreases continuously throughout the reaction,

equation (e) would then suggest that the rate of loss of weight, per unit weight of residue, should increase as pyrolysis proceeds. It has been shown both experimentally (11) and theoretically (134), however, that, for a process which involves random chain scission, the change in molecular weight of the residue is small during the later stages of the reaction. In this work, since the system did not attain thermal equilibrium until 8-10 minutes after the introduction of the sample into the reaction vessel (figure 12), only the later stages of the reaction were studied, and if the associated variation of m is small, then equation (e) adequately describes the results obtained.

From equation (d) the overall activation energy for the rate of loss of weight, E_0 kcal mole⁻¹, is given by:

$$E_0 = E_2 + \frac{1}{2}(E_1 - E_3) \quad (f)$$

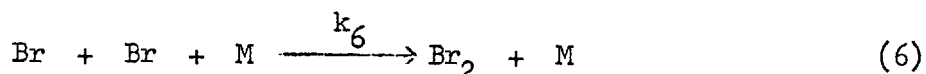
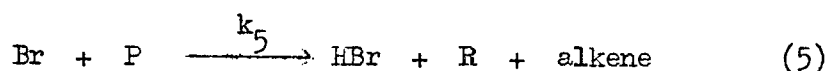
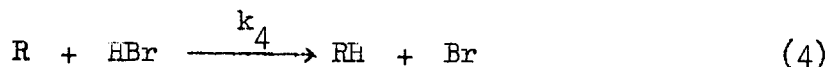
where E_1 , E_2 and E_3 are the activation energies of reactions (1), (2) and (3) respectively. The experimental value of E_0 is about 70 kcal mole⁻¹ (table 16). If it is assumed that E_1 is equal to the dissociation energy of the C-C bonds in the polymer and that $E_3 = 0$, then E_2 (calculated from equation (f)) is approximately 33 kcal mole⁻¹. The use of the experimentally determined value of E_0 in this calculation assumes that the variation of temperature does not significantly affect the values of m and p which appear in equation (d).

It was assumed in the above discussion that the rate of loss of weight of the polymer in thermal degradation is chemically controlled. It is possible, however, that the rate of loss of weight is controlled by the rate of evaporation of volatile products from the polymer. For

sample weights less than 10 mg., the rate of loss of weight was not influenced by variation of the surface area-sample weight ratio (figure 13, table 11) although, since the sample thickness was not rigidly controlled, the conclusion that the rate of loss of weight is not diffusion controlled may not be valid. Equations (d) and (f) would not be relevant to a system in which the rate of loss of weight is evaporation controlled. In the absence of direct evidence of evaporation control, however, the value of E_2 obtained from equation (f) is used later in the discussion. It must be emphasised in this context, however, that the discussion of the influence of hydrogen bromide, in terms of the rate of bond scission of polymer molecules (which follows below), is still thought to be valid since the sample weights and surface areas of the polymer samples decomposed in the presence and absence of additive were identical. Thus, with identical forms of sample, it is difficult to account for the reduced loss of weight in the presence of hydrogen bromide unless it is supposed that the additive acts by reducing the rate of bond scission within the polymer.

(c) The influence of hydrogen bromide on the reaction mechanism

It is proposed that the following additional reactions occur in the presence of hydrogen bromide:



Reaction (5), involving hydrogen abstraction and chain scission is similar to reaction (2) described previously. Reaction (6) (which, since it involves the combination of atoms, requires a 'third body', M) and reaction (7) are termination reactions. At the temperatures concerned, hydrogen bromide would be rapidly eliminated from the bromoalkane formed initially by the combination of a bromine atom and an alkyl radical in reaction (7).

It is first necessary to determine whether the rate at which radicals undergo reaction (4) is comparable with the rate at which they undergo reaction (2). From the relevant bond strengths, reaction (4) is found to be approximately 13 kcal mole⁻¹ exothermic. The activation energy for a reaction of the type: $\text{Br} + \text{RH} \longrightarrow \text{HBr} + \text{R}$, is given by $E = 0.91\Delta H + 4.3 \text{ kcal mole}^{-1}$, where ΔH is the endothermicity of the reaction (135). Thus the activation energy for the reverse of reaction (4) given by this expression is 16 kcal mole⁻¹. Since reaction (4) is 13 kcal mole⁻¹ exothermic, the activation energy for reaction (4) is therefore 3 kcal mole⁻¹. Thus, for a given concentration of alkyl radicals, the ratio of the rates of reactions (4) and (2) is given by:

$$r_4/r_2 = (A_4/A_2) \cdot \exp(30,000/RT) \cdot [\text{HBr}]/[\text{H}_2\text{O}]$$

where A_2 and A_4 are the relevant pre-exponential factors. Thus, at 430°C and with $[\text{H}_2\text{O}] = 140 \text{ mole litre}^{-1}$ (p.211),

$$r_4/r_2 = (A_4/A_2)[\text{HBr}] \cdot 10^7 \quad .$$

The concentration of hydrogen bromide in the polymer under the conditions used is believed to be of the order of 10^{-3} mole litre $^{-1}$ (p.211). Even if the concentration of hydrogen bromide is considerably less than that estimated, the reaction of alkyl radicals with hydrogen bromide probably competes significantly with attack of alkyl radicals on the polymer, provided that A_4 is not appreciably less than A_2 . It is thought that the latter condition will hold since it is probable that A_4 will be greater than A_2 ; thus reaction (4) is a simple bimolecular transfer reaction whereas reaction (2) is a more complex transfer and decomposition step.

If it is assumed that steady state concentrations of both R and Br are attained and that the concentration of hydrogen bromide in the polymer remains constant throughout the reaction, the following results are obtained:

$$k_1[P] = k_3[R]^2 + k_6[M][Br]^2 + k_7[Br][R] \quad (g)$$

$$r_b = k_2[R][H_2O] + k_5[Br][H_2O] \quad (h).$$

If the rate constants for the termination reactions are related by the parameters β and γ , where,

$$[M]k_6 - k_3 = \beta \quad \text{and} \quad k_7 - 2k_3 = \gamma$$

then equation (g) gives:

$$[R] + [Br] = \left[\frac{k_1[P] - \beta[Br]^2 - \gamma[R][Br]}{k_3} \right]^{\frac{1}{2}} \quad (j).$$

The two reactions, (2) and (5), which give rise to bond scission in the presence of hydrogen bromide are of a similar nature; each involves the scission of both a secondary carbon-hydrogen bond and a carbon-carbon bond in the polymer molecules. It is assumed, therefore, as a first approximation, that $k_2 = k_5$. Thus equation (h) becomes:

$$r_b = k_2 [H_2O]([R] + [Br]) \quad (k).$$

Note that, since it is assumed that $[R]$ and $[Br]$ are constant, equation (k) predicts that the rate of loss of weight in the presence of hydrogen bromide is proportional to the weight of the residue (this conclusion follows from an argument similar to that outlined for the pyrolysis of the polymer in the absence of additives on p.214); this was observed to be the case (figures 26,27).

It is evident from a comparison of equations (b) and (k) that hydrogen bromide will reduce the rate of loss of weight of the polymer if $([R] + [Br])$ in the presence of the additive is less than $[R]$ in its absence. This will be the case (compare equations (a) and (j)) provided that the quantity $\left[\beta [Br]^2 + \gamma [R][Br] \right]$ is positive. This condition cannot be fully elucidated since a determination of the appropriate radical concentrations is not possible. It is obvious, however, that the above quantity can in no circumstances be positive if both β and γ are negative. Thus one of the conditions for an inhibition of loss of weight is that at least one of the parameters, β and γ , should be positive. The physical significance of this condition is that the rate constants for termination reactions involving bromine atoms (where for reaction (6), $k_6[M]$ is taken as the 'rate

constant' since $[M]$ is constant in the polymer) should be greater than for the termination reaction involving two large alkyl radicals. The detailed discussion of this possibility is, however, postponed until after the discussion of the validity of the assumption that $k_2 = k_5$.

The relative rates of reactions (2) and (5) are discussed in terms of their pre-exponential factors and activation energies. From the values of the bond strengths of R-H (primary) and H-Br it is found that reaction (2) is 13 kcal mole⁻¹ more exothermic than reaction (5). Thus E_5 is probably greater than E_2 although the difference is quite small. This factor taken in isolation would lead to the conclusion that $k_2 > k_5$. A_2 and A_5 are compared by considering the nature of the reaction species and of the intermediate complexes formed. Reaction (2) involves the attack of a polymer molecule by a large alkyl radical whereas reaction (5) involves the attack of a polymer molecule by a bromine atom. Thus, from consideration of the sizes of the attacking radicals, the loss of translational entropy in forming the intermediate complex in reaction (2) is probably considerably greater than the corresponding loss in reaction (5). Furthermore, there is almost certainly a loss of rotational entropy involved in the formation of the intermediate complex in reaction (2) due to restricted rotation, about the point of attack, of that part of the complex derived from the attacking radical; there is no equivalent loss in reaction (5) where the radical species is an atom. Thus, if the entropy of activation is less for reaction (2) than for reaction (5), $A_5 > A_2$. If this factor is more significant than the difference in the activation energies of these two reactions (which will probably be the case), $k_5 > k_2$. Thus,

if the total radical concentration, $([R] + [Br])$, in the polymer is not less than the radical concentration in the absence of additive, $[R]$, the rate of bond scission would be increased by the presence of hydrogen bromide.

The influence of hydrogen bromide on the rate of loss of weight will depend on which of the two competing effects is of greater significance. These effects are:

- (i) a decrease in the total radical concentration caused by a possible increase in the rate of chain termination;
 - (ii) an increase in the rate of chain propagation for a given radical concentration, due to the presence of bromine atoms in the system.
- The first of these effects is now discussed in greater detail.

It is instructive, in the first instance, to consider the relative magnitudes of k_3 and $k_6[M]$ in the light of data obtained for the relevant reactions in the gas phase. From data determined for k_6 at different temperatures, with argon as the third body, (136), it is found that, at 430°C , k_6 is of the order of $10^9 \text{ litre}^2 \text{ mole}^{-2} \text{ sec}^{-1}$. If it is assumed that the data for the gas phase reaction may be extrapolated to the conditions which exist in the polymer, and that each CH_2 unit in the polymer acts as a third body for the recombination of bromine atoms, then, since $[\text{CH}_2] = 70 \text{ mole litre}^{-1}$, $k_6[M] = 10^{11} \text{ litre mole}^{-1} \text{ sec}^{-1}$. The rate constant for the recombination of ethyl radicals in the gas phase at 430°C has been estimated from published data (137) and is of the order of $10^{10} \text{ litre mole}^{-1} \text{ sec}^{-1}$. The influence of radical and molecular size on the rates of radical reactions was discussed previously when the rates of reactions (2) and (5) were compared. The arguments used in that

discussion, in terms of entropy of activation, would suggest that k_3 , the rate constant for a termination reaction involving radicals of considerable size, is considerably less than the rate constant for the recombination of ethyl radicals. Thus, in the absence of any effect of the reaction medium, it appears that, for equivalent concentrations of radicals, the rate of recombination of bromine atoms is greater than that of two large alkyl radicals. The influence of the reaction medium on the relative rates of the termination reactions is now discussed.

The present knowledge of the kinetics of reactions in polymers at temperatures at which they undergo degradation is such that it is difficult to estimate the effect of such a medium on the relative rates of the termination reactions (3), (6) and (7) except in the light of effects which are known to occur in polymerisation reactions. Thus the autoacceleration of the polymerisation of poly(methyl methacrylate) (138) is almost certainly due to a decrease in the rate of the termination reaction (139). This effect is thought to be due in part to the size of the reacting radicals and in part to the viscosity of the reaction medium. Although the rate of the reaction of large radicals with one another is reduced, the rate at which they react with small monomer molecules is relatively little affected by the increasing viscosity of the medium and this accounts for the phenomenon of autoacceleration. Such a difference between the rate constants for the reactions of small and large species in a viscous phase would, in the case of degradation of polyethylene in the presence of hydrogen bromide, favour termination by reactions involving bromine atoms.

From the above discussion, it is evident that $k_6[M]$ and k_7 are

probably considerably greater than k_3 . Thus the influence of hydrogen bromide in decreasing the rate of loss of weight of polyethylene may be explained by supposing that the increased rate of chain termination, and hence the reduced radical concentration, is more significant than the probability that $k_5 > k_2$. In other words, (i) is the more significant of the effects summarised on p. 221.

The presence of hydrogen bromide increased the rate of the gas phase pyrolysis of the volatile degradation products. If it is assumed that the mechanism whereby hydrocarbons undergo degradation in the gas phase is similar to that proposed for the corresponding reactions in the polymer, the influence of the additive on the two reactions may be related in the following way. In the gas phase, the value of $[M]$ is obviously several orders of magnitude less than the corresponding value in the polymer phase. Thus, $k_6[M]$ is considerably less in the gas phase than in the polymer phase. On the other hand, since the average chain length of radicals in the gas phase is less than in the polymer, the value of k_3 in the gas phase will be greater than that in the polymer. Moreover, it was suggested that in the polymer, termination reactions involving bromine atoms were favoured, with respect to termination involving two alkyl radicals, by the nature of the medium. The possibility of such an effect does not exist in the gas phase, so that this basis of comparison also suggests that k_3 for the reaction in the gas phase is greater than for that in the polymer. The conclusion reached previously in the discussion of the polymer reaction that, for equivalent concentrations of bromine atoms and alkyl radicals, the rate of chain scission by the bromine atoms is greater than by alkyl

radicals applies also in the gas phase reaction. Thus, if the reduction of $[M]$ and the increase in k_3 in the gas phase (compared with the values of these quantities appropriate to the polymer reaction) are such that β and γ are negative, the rate of pyrolysis of hydrocarbons in the gas phase will certainly be increased by hydrogen bromide. The parameters β and γ , although reduced with respect to the values appropriate to the polymer reaction, may, however, still be positive. In the latter case, the influence of hydrogen bromide will be to promote the degradation of hydrocarbons if factor (ii) (p.221) predominates in the gas phase reaction.

It is not possible to discuss quantitatively the effects described in the discussion above. The discussion does explain qualitatively, however, how hydrogen bromide may promote the degradation of the volatile decomposition products of polyethylene in the gas phase and yet decrease the rate at which the polymer itself is degraded.

D The relationship between the effects of hydrogen bromide on the pyrolysis and oxidation of polyethylene

The work which has been described on the reaction between polyethylene and oxygen and the influence of hydrogen bromide on this reaction, represents one of the first attempts to investigate such a system and the rudimentary nature of this work does not allow a detailed discussion of the elementary reactions involved. In the following discussion, therefore, such conclusions as are drawn must be regarded, at this stage, as somewhat tentative.

The relation between the final pressure increase and initial sample weight (figure 43) suggests that, if the nature of the final product mixture in the gas phase is the same for each sample weight used, the final extent of oxidation is independent of initial sample weight in the range investigated. Since, for one of the sample weights used, the final products of oxidation were almost entirely water, carbon monoxide and carbon dioxide (table 28), it appears that, in an excess of oxygen, the carbon chains originally present in the polymer sample are completely degraded to molecules containing single carbon atoms.

The rate of pressure change gave some indication of the combined rates of the reactions of oxygen with the polymer and with product molecules in the gas phase. The rate of pressure change is most likely to indicate the rate of the direct reaction between oxygen and the polymer in the initial, rather than the later stages of the reaction, since, in the initial stages, the concentration of products in the gas phase is relatively small. Thus the initial rate of pressure increase is used to discuss the influence of sample size on the rate of the reaction between the polymer and oxygen. For a given oxygen concentration, provided that oxygen is distributed homogeneously throughout the polymer, the relative concentrations of polymer and oxygen are not influenced by sample weight. However, since the volume of the sample is directly proportional to its weight, the rate of the initial reaction should be proportional to the weight of the polymer sample. If, on the other hand, the rate of the primary reaction is controlled by the rate of diffusion of oxygen into the polymer, or the pressure increase is controlled by the rate of diffusion of products from the

polymer, a linear relationship between sample weight and rate of pressure increase would not be observed. If it is assumed that, in these experiments, the thickness of the polymer sample was proportional to sample weight, the results obtained suggest that only when the sample weight is greater than about 8-10 mg. does the question arise of the reaction being diffusion controlled (figure 44). The possibility of diffusion control for sample weights of less than 8 mg. cannot be completely eliminated, however, since the surface area of the polymer sample was not strictly controlled. In view of this uncertainty, the results from pressure change measurements are best used for a comparative discussion of the oxidation reactions in the presence and absence of hydrogen bromide (under otherwise identical conditions of sample weight and initial oxygen concentration) rather than for a discussion of the kinetics of the oxidation reaction in the absence of additives.

Hydrogen bromide increases the rate of pressure increase observed (figures 47,48). It is known that hydrogen bromide increases the rate of oxidation of hydrocarbons in the gas phase (96-100). That such an effect contributes to the increased rate of pressure increase is confirmed by the results obtained from product analysis work. Thus, in the absence of additive, the yield of volatile hydrocarbons increases to a maximum after about 30 seconds' oxidation and thereafter decreases (figure 51). This behaviour presumably results from two competing processes. The first is the production of a given hydrocarbon by oxidative degradation of the polymer and its volatile degradation products; the second is the oxidation of that hydrocarbon in the gas phase. In the experiments where hydrogen bromide was used as the

additive, no maximum concentration of a given hydrocarbon was directly observed since the concentration of each hydrocarbon decreased continuously (figure 51). The maximum concentrations of each hydrocarbon in experiments involving hydrogen bromide were, however, probably less than the corresponding concentrations observed in the absence of the additive. Thus hydrogen bromide either increases the rate of oxidation for each hydrocarbon or decreases the rate of formation. Certainly the rate of oxidation of volatile hydrocarbons is increased by the presence of this additive and, since the rate of loss of weight of the polymer is decreased by hydrogen bromide (figures 49,50, table 26), the rate of formation of hydrocarbons may also be reduced.

The smaller overall pressure increase and the subsequent pressure decrease, which were sometimes observed in the presence of hydrogen bromide (table 25), may be due to an increase in the rate of the reaction;



In support of this hypothesis, it was found in this work that, for a given time of reaction, the quantity of carbon dioxide formed was increased by the presence of hydrogen bromide (figure 53).

Bromomethane was observed to be a product of the oxidation of polyethylene in the presence of hydrogen bromide (figure 58); no other brominated hydrocarbons were detected. No further investigation of the formation of bromomethane was made, but it is worth noting that bromomethane is the most thermally stable of the monobromoalkanes (this point is discussed in detail on pp. 198,199) and is, therefore, the most likely of these compounds to exist in appreciable concentrations at 430°C.

The reduction of the rate of loss of weight of polyethylene observed with hydrogen bromide present (figures 49,50, table 26) may be due to a number of effects which are listed and discussed below.

(i) Combination between the polymer and oxygen may be accelerated by the presence of hydrogen bromide or combination between bromine and the polymer may occur. No conclusion may be reached on this point since no elemental analysis of the residue was carried out.

(ii) For a given time of reaction, the concentration of oxygen available for the oxidation of the polymer may be reduced by an increased rate of reaction of oxygen in the gas phase. Although this may account for the reduction in the rate of loss of weight in the intermediate stages, it is unlikely to account for the reduction in the rate of loss of weight observed in the initial stages of the reaction.

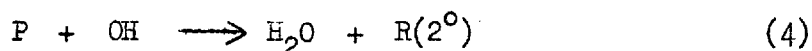
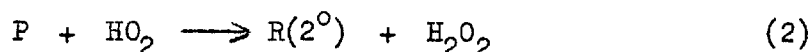
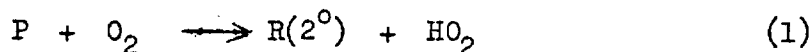
(iii) Hydrogen bromide may increase the rate of cross-linking in the residue and hence reduce the rate of formation of volatile products. It may perhaps be relevant that hydrogen bromide increased the weight of the involatile residue which remained after complete oxidation (figure 49, table 26).

(iv) The reduction in the rate of loss of weight may be due to a chemical influence of hydrogen bromide on the reactions involved in the oxidative degradation of polyethylene. Despite the uncertainties regarding the effects (i) - (iii) outlined above, a brief discussion of the possible chemical influence of hydrogen bromide on the oxidative degradation of polyethylene is thought desirable. First, therefore, the nature of the oxidative degradation reaction in the absence of additives is discussed.

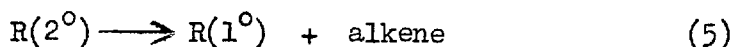
In experiments in the absence of hydrogen bromide, the maximum concentration of hydrocarbons in the gas phase was found to be present at that stage of the reaction at which the polymer residue ceased to lose weight. From this correlation it appears that a considerable proportion of each hydrocarbon results from a direct reaction between the polymer and oxygen. It was also observed, however, that the concentration of alkanes present during the first 30 seconds' oxidation was proportional to the weight of polymer volatilised, whereas for alkenes, the quantity increased during this period of the reaction (figure 52). This may suggest that, as the volatile products of polymer degradation accumulate in the gas phase, a greater proportion of the alkenes results from reactions occurring in the gas phase. Thus, of the products recorded, the alkanes appear the most likely products formed directly from the reaction between the polymer and oxygen. If this is the case, it is of interest that the yields of alkanes obtained by the oxidation of polyethylene are comparable with those during the thermal degradation of the polymer (compare table 27 with table 21). Moreover, in both thermal and oxidative degradation, the concentration of a given alkane in the gas phase is a linear function of polymer weight loss (figures 34-37,52). Since thermal degradation proceeds by a process of random chain scission, this evidence may suggest that oxidative degradation occurs by such a process. Such a conclusion must, however, be tentative at this stage since a complete volatile product spectrum was not obtained during the initial stages of oxidation. Nevertheless, the observations summarised above, taken with the deduction that oxidation in the gas phase continued for some time after oxidation of

the polymer itself was complete (compare the results shown in figures 42,45,51,53-55 with those shown in figure 49), lead to the following general description of the oxidative degradation of polyethylene. The main process occurring in the polymer is the random chain scission of the polymer molecules by oxygen to yield volatile hydrocarbons which are then extensively oxidised in the gas phase.

The mechanism of oxidation of polyethylene at temperatures of about 200°C resembles closely the mechanism by which hydrocarbons are oxidised in the gas phase at comparable temperatures (section C.3(a) of the Introduction). Similarly, the following mechanism for the random degradation of polyethylene by oxygen at 430°C is, in part, based on a mechanism which has been proposed for the oxidation of straight chain hydrocarbons in the gas phase in the appropriate temperature range (53).



The secondary radicals, $R(2^\circ)$, formed in reactions (1), (2) and (4) may then decompose to yield primary radicals, $R(1^\circ)$:

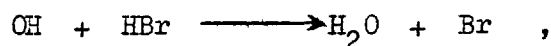


or this decomposition may be part of a unified mechanism involving reactions (1), (2) or (4). Primary alkyl radicals formed in this way

may react with other polymer molecules, causing chain scission, and so initiate a chain reaction identical to that proposed for the thermal degradation of the polymer (reaction (2), p. 212).

The reaction sequence outlined above involves oxygen acting essentially by increasing the rate of chain initiation, compared with thermal degradation, but is otherwise similar to the mechanism for the pyrolysis of polyethylene. Thus the reaction may be described simply as the oxygen-catalysed pyrolysis of the polymer.

In the presence of hydrogen bromide, therefore, the rate of chain scission may be reduced in a manner exactly analogous to that by which the rate of thermal degradation is reduced. In addition, retardation may also result from a reaction between hydrogen bromide and any of the species responsible for initiation, e.g.,



provided that, in this case, the reaction:



is less frequent than reaction (4).

Hydrogen bromide may, however, increase the rate of initiation if the reaction:



occurs more readily than reaction (1); such a mode of initiation is thought to be responsible for the catalysis of the gas phase oxidation of hydrocarbons by hydrogen bromide (101).

On the basis of this scheme, therefore, the overall influence of hydrogen bromide on the oxidation reaction depends on the relative

importance of the reactions in which this additive may participate. It is of interest, however, that the reaction sequence proposed does allow inhibition of the oxidation reaction by hydrogen bromide in a manner similar to that already described in connection with the thermal degradation of the polymer.

E The significance of the present work with respect to the flammability of polyethylene

When a polymer burns, the fuel is supplied to the flame by thermal degradation of the polymer under the influence of heat supplied from the flame front. There may also be a contribution to the fuel by oxidative degradation at the periphery of the flame. Thus the flammability of polyethylene would be reduced by any agency which reduces the flammability of the products of thermal degradation of polyethylene or reduces the rate at which fuel is supplied to the flame. This work has shown that hydrogen bromide causes no significant change in the nature of the products of thermal degradation of the polymer. This additive does, however, reduce the rate of thermal degradation of polyethylene. Moreover, the effect is quite noticeable with relatively small concentrations of hydrogen bromide in the degrading polymer (less than 10^{-3} mole litre⁻¹) and the inhibition increases with the concentration of hydrogen bromide. Thus, if a solid additive is incorporated into a sample of polyethylene which releases an appreciable quantity of hydrogen bromide, the flammability of the polymer may be reduced by a reduction in the rate at which fuel is supplied to the flame. This work has also shown that it is possible that hydrogen bromide reduces the rate of oxidative degradation of the polymer. Thus, if in

burning polyethylene oxidative degradation contributes significantly to the supply of fuel, the incorporation of a suitable bromine-containing additive may reduce the flammability of the polymer by also reducing the rate of oxidative degradation.

Work on the influence of organic bromides on the thermal degradation showed that this reaction was retarded only by those compounds which decompose to yield hydrogen bromide under the experimental conditions used. Thus, in the light of this work, the following general observations may be made on the reduction of the flammability of polyethylene by solid bromine-containing compounds. For the compound to have the maximum possible effect, its thermal stability should be such that hydrogen bromide is released in the temperature range 400-500°C. From previous discussion it does not appear probable that direct bromination of polyethylene would meet this requirement since hydrogen bromide is released at a somewhat lower temperature than that at which polyethylene undergoes degradation. In practice, an additive may still be effective if hydrogen bromide is formed at less than 400°C because the conditions may be such that the gas passes through the degradation phase of the polymer on being released. The effect is less certain in this case, however, than in the case where the thermal stabilities of the polymer and the additive are comparable.

One other possible effect of hydrogen bromide on the flammability of polyethylene is worth noting. In the course of this work, the rate of heat transfer in a reaction vessel containing hydrogen bromide was found to be less than that observed when the reaction vessel contained helium or nitrogen. If, at the instant of ignition of a

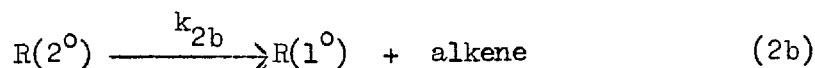
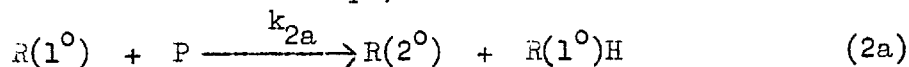
sample of polyethylene in which a bromine-containing additive is incorporated, an appreciable concentration of hydrogen bromide is released, it is possible that the rate of heat transfer between the flame front and the polymer may be reduced to such an extent that the flame is extinguished by a reduction in the supply of fuel.

Hydrogen bromide may also reduce the rate of flame propagation in burning polyethylene. At present no data are available regarding the influence of hydrogen bromide on the flame of a hydrocarbon mixture comparable to that supplied by the thermal degradation of polyethylene. Thus it is not possible to decide, in the event of a reduction by an additive of the flammability of polyethylene, whether the effect discovered in this work predominates over the possible influence of hydrogen bromide on the rate of reactions occurring in the flame.

APPENDIX

1. The nature of the propagation reaction in thermal degradation

The nature of reaction (2) in the proposed reaction scheme (p. 212) may be discussed in the light of the value obtained for its activation energy. In this reaction, hydrogen abstraction by the primary alkyl radical occurs simultaneously with chain scission in the polymer molecule from which hydrogen is abstracted. An alternative process involves two distinct steps, viz.



where $R(1^\circ)$ and $R(2^\circ)$ represent primary and secondary alkyl radicals respectively. If it is assumed that steady state conditions prevail, the inclusion of (2a) and (2b), rather than (2), in the reaction scheme gives the equations:

$$r_b = k_{2a}[H\ 2^\circ][R(1^\circ)] \quad (m)$$

$$E_o = E_{2a} + \frac{1}{2}(E_1 - E_3) \quad .$$

On the basis of the previous calculation (p.215), both of the alternative reactions, (2) and (2a), apparently have an activation energy of 33 kcal mole⁻¹.

Reaction (2a) is an exothermic reaction involving hydrogen transfer between a primary alkyl radical and a secondary hydrogen atom in a hydrocarbon. Application of the Hirschfelder rule (140) to a

reaction of this nature gives an activation energy of about 5 kcal mole⁻¹. It is not possible to estimate the activation energy of reaction (2). However, since in reaction (2) two bonds must be weakened considerably before any new bond is formed, the activation energy for reaction (2) will be higher than that for reaction (2a). Thus it is thought that an activation energy of 33 kcal mole⁻¹ would be more likely to apply to reaction (2) than to reaction (2a). On the basis of this purely empirical argument alone, reaction (2) has been used in the proposed reaction scheme.

It must be emphasised that the choice between these alternative reaction schemes in no way affects the qualitative argument used in the discussion of the reaction in the presence and absence of hydrogen bromide. Thus, in each of the alternative schemes, primary radicals react with polymer molecules and it is the concentration of primary radicals which appears in the relevant equations (compare equations (b) and (m)). Finally it is noted that in previous work no serious discussion of the nature of the propagation step appears to have been attempted. In one case, for example, reaction (2) has been proposed without further discussion (21) and in another case (22), where reactions (2a) and (2b) have been proposed, it has been assumed that reaction (2b) is fast compared with reaction (2a) so that in the reaction mechanism the propagation step may be effectively written as reaction (2). The validity of this assumption was not discussed.

2. Influence of volume change on the kinetics of the thermal degradation of polyethylene

It has been assumed that none of the radicals present in the

polyethylene sample are lost by evaporation (p.213). Thus, in the application of steady state conditions to the concentration of radicals, the effect of the volume change which accompanies the thermal degradation reaction must be taken into account. This discussion attempts to evaluate the magnitude of such an effect.

Let N be the total number of moles of alkyl radicals after a time t seconds in a polymer sample of weight w gm. and density d gm. litre⁻¹.

$$\text{Thus,} \quad [R] = Nd/w \quad \text{mole litre}^{-1}$$

$$\text{and,} \quad -d[R]/dt = Nd(1/w)^2(dw/dt) \quad \text{mole litre}^{-1}\text{sec}^{-1}$$

$$\text{or} \quad -d[R]/dt = [R](1/w)(dw/dt) \quad \text{mole litre}^{-1}\text{sec}^{-1}$$

Thus the equation derived for the reaction sequence proposed becomes:

$$2k_1[P] - [R](1/w)(dw/dt) - 2k_3[R]^2 = 0$$

$$\text{whence,} \quad [R] = \frac{-(1/w \cdot dw/dt) + \left[(1/w \cdot dw/dt)^2 + 16k_1k_3[P] \right]^{1/2}}{4k_3}$$

It was observed experimentally that $(-1/w \cdot dw/dt)$ was constant for the later stages of the pyrolysis reaction and was of the order of 10^{-3} sec^{-1} at 430°C (table 13). If the number average chain length of the polymer sample for that part of the reaction studied is of the order of 100 and the density of the polymer is of the order of 1000 gm. litre⁻¹, then $[P]$ is of the order of 1 mole litre⁻¹.

If $k_1 = A_1 \exp(-E_1/RT) \text{ sec}^{-1}$ and A_1 is of the order of 10^{13} sec^{-1} (the

'normal' pre-exponential factor for unimolecular reactions), and $E_1 = 75 \text{ kcal mole}^{-1}$, then, at 430°C , k_1 is of the order of $10^{-10} \text{ sec}^{-1}$. Thus $16k_1k_3[P] = 10^{-9}k_3 \text{ sec}^{-2}$. It is clear, therefore, that if k_3 is of the order of 10^5 - $10^6 \text{ litre mole}^{-1}\text{sec}^{-1}$, the error involved in neglecting the influence of changing volume on the kinetic analysis of the thermal degradation reaction will not be large.

The value of k_3 for the termination reaction involving two large alkyl radicals cannot be calculated with certainty. The rate constant for the recombination of two ethyl radicals in the gas phase at 430°C is of the order of $10^{10} \text{ litre mole}^{-1}\text{sec}^{-1}$ (p. 221). For the combination of the large radicals involved in the termination reaction in the photodegradation of poly(methyl methacrylate) at 200°C , where the reaction phase is of high viscosity, the rate constant is of the order of $10^4 \text{ litre mole}^{-1}\text{sec}^{-1}$ (141). In the present case, the value of k_3 will lie between these two extreme values and it is probably greater than $10^6 \text{ litre mole}^{-1}\text{sec}^{-1}$. Thus it is not thought that, by neglecting the influence of changing volume, the validity of the argument is seriously affected. It must be borne in mind, however, that if k_3 were less than $10^5 \text{ litre mole}^{-1}\text{sec}^{-1}$ the argument would be so affected. It is certainly surprising that few authors have considered such an effect when proposing a steady state concentration of radicals in the analysis of polymer degradation under conditions where loss of weight of the polymer occurs.

REFERENCES

1. C.E.H.Bawn, Chem.Brit., 1, 465 (1965).
2. N.Grassie and H.W.Melville, Proc.Roy.Soc., A 199, 1 (1949).
3. N.Grassie and H.W.Melville, Proc.Roy.Soc., A 199, 39 (1949).
4. S.L.Madorsky, 'Thermal Degradation of Organic Polymers' (Interscience Publishers, 1964) p.4.
5. S.L.Madorsky and S.Straus, J.Research Natl.Bur.Standards, 63A, 261 (1959).
6. H.H.G.Jellinek, J.Polymer Sci., 4, 13 (1949).
7. S.L.Madorsky, J.Polymer Sci., 9, 133 (1952).
8. D.A.Anderson and E.S.Freeman, J.Polymer Sci., 54, 253 (1961).
9. W.G.Oakes and R.B.Richards, J.Chem.Soc., 2929 (1949).
10. S.L.Madorsky, S.Straus, D.Thompson and L.Williamson, J.Research Natl.Bur.Standards, 42, 499 (1949).
11. L.A.Wall, S.L.Madorsky, D.W.Brown, S.Straus and R.Simha, J.Amer.Chem.Soc., 76, 3430 (1954).
12. H.W.Thompson and P.Torkington, Proc.Roy.Soc., A 184, 3 (1945).
13. S.L.Madorsky and S.Straus, J.Research Natl.Bur.Standards, 53, 361 (1954).
14. S.L.Madorsky and S.Straus, Soc.Chem.Ind., Monograph No.13, 60 (1961).
15. S.L.Madorsky, Soc.Plastic Engrs.J., 17, 665 (1961).
16. S.L.Madorsky, 'Thermal Degradation of Organic Polymers' (Interscience Publishers, 1964) p.24.
17. A.Atherton, J.Polymer Sci., 5, 378 (1950).
18. S.L.Madorsky, J.Research Natl.Bur.Standards, 62, 219 (1959).
19. O.F.Rice and K.K.Rice, 'The Aliphatic Free Radicals' (Johns Hopkins Press, Baltimore, 1935).
20. R.Simha, J.Applied Phys., 12, 569 (1941).
21. R.Simha, L.A.Wall and P.J.Blatt, J.Polymer Sci., 5, 615 (1950).

22. R.Simha and L.A.Wall, J.Phys.Chem., 56, 707 (1952).
23. R.Simha, Trans. N.Y. Acad.Sci., 14, 151 (1952).
24. N.Grassie and H.W.Melville, Proc.Roy.Soc., A 199, 14 (1949).
25. S.L.Madorsky, 'Thermal Degradation of Organic Polymers' (Interscience Publishers, 1964) p.95.
26. H.Staudinger and A.Steinhofer, Ann., 517, 35 (1935).
27. N.Grassie and H.W.Melville, Proc.Roy.Soc., A 199, 24 (1949).
28. L.A.Wall and J.D.Michaelsen, J.Research Natl.Bur.Standards, 56, 27 (1956).
29. H.H.G.Jellinek and L.B.Spencer, J.Polymer Sci., 8, 573 (1952).
30. G.G.Cameron and N.Grassie, Polymer, 2, 367 (1961).
31. S.Straus and L.A.Wall, J.Research Natl.Bur.Standards, 65A, 221 (1961).
32. H.C.Beachell and S.P.Nemphos, J.Polymer Sci., 21, 113 (1956).
33. N.T.Notley, Trans. Faraday Soc., 58, 66 (1962).
34. T.L.Cottrell, 'The Strengths of Chemical Bonds' (Butterworths, London, 1958) p.270.
35. C.F.Cullis, F.R.F.Hardy and D.W.Turner, Proc.Roy.Soc., A 244, 573 (1958); A 251, 265 (1959).
36. C.N.Satterfield and R.F.Wilson, Ind.Eng.Chem., 46, 1001 (1954).
37. J.W.Falconer and J.H.Knox, Proc.Roy.Soc., A 250, 493 (1959).
38. A.Fish, Quart.Rev., 18, 243 (1964).
39. A.P.Zeelenberg and H.W. de Bruijn, Combustion and Flame, 9, 281 (1965).
40. C.F.Cullis, A.Fish, M.Saeed and D.L.Trimm, Proc.Roy.Soc., A 289, 402 (1966).
41. J.Cartlidge and C.F.H.Tipper, Proc.Roy.Soc., A 261, 388 (1961).
42. T.Berceś and A.F.Trotman-Dickenson, J.Chem.Soc., 348 (1961).
43. C.P.Fenimore and G.W.Jones, J.Phys.Chem., 65, 2200 (1961).
44. R.Shaw and A.F.Trotman-Dickenson, J.Chem.Soc., 3210 (1960).

45. J.Bardwell, Proc.Roy.Soc., A 207, 470 (1951).
46. A.D.Kirk and J.H.Knox, Trans. Faraday Soc., 56, 1296 (1960).
47. D.E.Hoare, J.B.Protheroe and A.D.Walsh, Trans. Faraday Soc., 55, 548 (1959).
48. R.R.Baldwin and D.Brattan, Eighth Symposium on Combustion (Williams and Wilkins, 1962) p.110.
49. R.G.W.Norrish, Discussions Faraday Soc., 10, 269 (1951).
50. J.H.Knox and R.G.W.Norrish, Proc.Roy.Soc., A 221, 151 (1954).
51. N.N.Semenov, Acta.physicochim. U.R.S.S., 18, 93 (1943).
52. D.A.Frank-Kamenetzky, 'Diffusion and Heat Exchange in Chemical Kinetics' (Princeton University Press, 1955).
53. C.F.Cullis, A.Fish and J.F.Gibson, Proc.Roy.Soc., A 284, 108 (1965).
54. A.D.Walsh, Ninth Symposium on Combustion (Academic Press, New York, 1963) p.1046.
55. A.Blundell and G.Skirrow, Proc.Roy.Soc., A 244, 331 (1958).
56. M.F.R.Mulcahy and M.J.Ridge, Trans.Faraday Soc., 49, 1297 (1953).
57. L.Bateman, Quart.Rev., 8, 147 (1954).
58. C.F.Cullis, A.Fish and D.W.Turner, Proc.Roy.Soc., A 262, 318 (1961); A 267, 433 (1962).
59. G.Skirrow and A.Williams, Proc.Roy.Soc., A 268, 537 (1962).
60. V.Kondratiev and M.Ziskin, Acta.physicochim, U.R.S.S., 6, 307 (1937).
61. L.Avramenko and V.Kondratiev, Acta.physicochim, U.R.S.S., 7, 567 (1937).
62. M.Gerstein, O.Levine and E.L.Wong, J.Amer.Chem.Soc., 73, 418 (1951).
63. C.F.Cullis, C.N.Hinshelwood, M.F.R.Mulcahy and R.G.Partington, Discussions Faraday Soc., 2, 111 (1947).
64. A.A.Westenberg and R.M.Fristrom, J.Phys.Chem., 64, 1393 (1960).
65. A.A.Westenberg and R.M.Fristrom, J.Phys.Chem., 65, 591 (1961).
66. R.M.Fristrom, C.Grunfelder and S.Favin, J.Phys.Chem., 64, 1386 (1960).

67. R.M.Fristrom, C.Grunfelder and S.Favin, J.Phys.Chem., 65, 587 (1961).
68. A.S.Gordon, S.R.Smith and J.R.McNesby, Seventh Symposium on Combustion (Butterworths Scientific Publications, London, 1959) p.317.
69. R.Friedman and J.A.Cyphers, J.Chem.Phys., 23, 1875 (1955).
70. R.M.Fristrom, R.Prescott and C.Grunfelder, Combustion and Flame, 1, 102 (1957).
71. R.M.Fristrom and A.A.Westenberg, Combustion and Flame, 1, 217 (1957).
72. R.M.Fristrom, W.H.Avery and C.Grunfelder, Seventh Symposium on Combustion (Butterworths Scientific Publications, London, 1959) p.304.
73. G.B.Skinner and R.A.Ruehrwein, J.Phys.Chem., 63, 1736 (1959).
74. C.P.Fenimore and G.W.Jones, J.Phys.Chem., 63, 1834 (1959).
75. C.P.Fenimore and G.W.Jones, J.Phys.Chem., 65, 2200 (1961).
76. C.P.Fenimore and G.W.Jones, J.Phys.Chem., 65, 1532 (1961).
77. A.Fish, Combustion and Flame, 8, 84 (1964).
78. C.P.Fenimore and G.W.Jones, Ninth Symposium on Combustion (Academic Press, New York, 1963) p.957.
79. Y.B.Zeldovitch and G.I.Barenblatt, Combustion and Flame, 3, 61 (1959).
80. C.Tanford and R.N.Pease, J.Chem.Phys., 15, 431, 861 (1947).
81. F.J.Weinberg, Proc.Roy.Soc., A 230, 331 (1955).
82. F.M.Rugg, J.J.Smith and R.C.Bacon, J.Polymer Sci., 13, 535 (1954).
83. J.P.Luongo, J.Polymer Sci., 42, 139 (1960).
84. H.C.Beachell and G.W.Tarbet, J.Polymer Sci., 45, 451 (1960).
85. V.M.Yur'ev, A.N.Pravednikov and S.S.Medvedev, Proc.Acad.Sci. USSR, 124, 335 (1959).
86. N.T.Notley, Trans.Faraday Soc., 60, 88 (1964).
87. M.B.Neiman, Russian Chem.Rev., 33, 13 (1964).
88. R.B.Mesrobian and A.V.Tobolsky, J.Polymer Sci., 2, 463 (1947).
89. B.Baum, J.Appl.Polymer Sci., 2, 281 (1959).

90. C.E.Boozer and G.S.Hammond, J.Amer.Chem.Soc., 76, 3861 (1954).
91. W.L.Hawkins, 'Oxidation and Combustion Reviews' Vol.I (Ed. C.F.H.Tipper, Elsevier, 1965) p.203.
92. G.W.Kennerly and W.L.Patterson, Ind.Eng.Chem., 48, 1917 (1956).
93. P.Volans, Paper presented at Plastics Institute Conference, 'Flame Resistance with Polymers', London, March, 1966.
94. S.L.Madorsky and S.Straus, J.Research Natl.Bur.Standards, 55, 223 (1955).
95. R.H.Dahms, Petroleum Refiner, 41, 132 (1962).
96. F.F.Rust and W.E.Vaughan, Ind.Eng.Chem., 41, 2595 (1949).
97. Z.K.Maizus and N.M.Emanuel, Dokl.Akad.Nauk, SSSR, 100, 115 (1955).
98. A.A.Babaeva, Z.K.Maizus and N.M.Emanuel, Izv.Akad.Nauk, SSSR, Otdel.Khim.Nauk, 1378, 1913 (1959).
99. E.R.Allen and C.F.H.Tipper, Proc.Roy.Soc., A 258, 251 (1960).
100. P.Hurst, G.Skirrow and C.F.H.Tipper, Proc.Roy.Soc., A 268, 405 (1962).
101. C.F.Cullis, A.Fish and R.B.Ward, Proc.Roy.Soc., A 276, 527 (1963).
102. J.H.Burgoyne and G.Williams-Leir, Proc.Roy.Soc., A 193, 525 (1948).
103. R.F.Simmons and H.G.Wolfhard, Trans.Faraday Soc., 51, 1211 (1955).
104. F.H.Garner, R.Long, A.J.Graham and A.Badakhshan, Sixth Symposium on Combustion (Reinhold Publishing Co., New York, 1957) p.802.
105. W.A.Rosser, H.Wise and J.Miller, Seventh Symposium on Combustion (Butterworths Scientific Publications, London, 1959) p.175.
106. A.Levy, J.W.Droege, J.J.Tighe and J.F.Foster, Eighth Symposium on Combustion (Williams and Wilkins, Baltimore, 1962) p.524.
107. R.Friedman and J.B.Levy, WADC Technical Report 56-568, Astia Document No. AD 110685.
108. E.C.Creitz, J.Research Natl.Bur.Standards, 65A, 389 (1961).
109. C.F.Cullis, A.Fish and R.B.Ward, Combustion and Flame, 7, 303 (1963).
110. U.S.Patent No. 2,676,946 (1954).

111. German Patent No. 1,050,999 (1954).
112. U.S. Patent No. 3,004,935 (1961).
113. J.Eichhorn, Paper presented at Los Angeles A.C.S. Symposium, 'Self-Extinguishing Polymers', April, 1963.
114. A.R.Ingram, J.Appl.Polymer Sci., 8, 2485 (1964).
115. J.Eichhorn, J.Appl.Polymer Sci., 8, 2497 (1964).
116. H.S.Booth, 'Inorganic Syntheses' Vol.I (McGraw Hill, New York, 1939) p.150.
117. A.Fish, Ph.D. Thesis (London, 1961).
118. W.H.McFadden, Anal.Chem., 30, 479 (1958).
119. H.P.Meissner and H.J.Schumacher, Z.physikal.Chem., A 185, 435 (1940).
120. E.T.Lessig, J.Phys.Chem., 36, 2325 (1932).
121. F.Daniels and P.L.Veltman, J.Chem.Phys., 7, 756 (1939).
122. P.J.Agius and A.Maccoll, J.Chem.Soc., 973 (1955).
123. A.Maccoll and P.J.Thomas, J.Chem.Soc., 979 (1955).
124. J.H.S.Green, A.Maccoll and P.J.Thomas, J.Chem.Soc., 184 (1960).
125. A.Maccoll and R.A.Ross, J.Amer.Chem.Soc., 87, 1169, 4997 (1965).
126. 'Handbook of Chemistry and Physics' (The Chemical Rubber Company, 1965) p.E-2.
127. I.J.Groome, Unpublished results.
128. T.L.Cottrell, 'The Strengths of Chemical Bonds' (Butterworths, London, 1958).
129. G.C.Fettis and J.H.Knox, 'Progress in Reaction Kinetics' (Ed. G.Porter, Pergamon Press, 1964) p.36.
130. J.H.Hildebrand and R.L.Scott, 'The Solubility of Nonelectrolytes' (Dover Publications Inc., New York, 1964) p.241.
131. R.B.Richards, Trans.Faraday Soc., 42, 10 (1946).
132. J.H.Hildebrand and R.L.Scott, 'The Solubility of Nonelectrolytes' (Dover Publications Inc., New York, 1964) p.424.

133. J.H.Hildebrand and R.L.Scott, 'The Solubility of Nonelectrolytes' (Dover Publications Inc., New York, 1964) p.266.
134. R.Simha and L.A.Wall, J.Polymer Sci., 6, 39 (1951).
135. G.C.Fettis and J.H.Knox, 'Progress in Reaction Kinetics' (Ed. G.Porter, Pergamon Press, 1964) p.33.
136. D.Britton and N.Davidson, J.Chem.Phys., 25, 810 (1956).
137. A.Shepp and K.O.Kutschke, J.Chem.Phys. 26, 1020 (1957).
138. G.V.Schulz and G.Harborth, Makromol.Chem., 1, 106 (1947).
139. M.S.Matheson, E.E.Auer, E.B.Bevilacqua and E.J.Hart, J.Amer.Chem.Soc., 71, 497 (1949).
140. J.O.Hirschfelder, J.Chem.Phys., 9, 645 (1941).
141. P.R.E.J.Cowley and H.W.Melville, Proc.Roy.Soc., A 211, 320 (1952).