

Some Aspects of the Degradation of Epoxide Resins

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Synopsis

This paper contains a description of the use of gas chromatography to examine the pyrolytic degradation of epoxide resins. The method depends on the pyrolysis of the material by use of an electrically heated filament, the difficulties of the method are examined and attempts to overcome them are described. The pyrolytic degradation of a resin based on the glycidyl ether of bisphenol-A hardened with 1,2-diaminoethane and also triethylenetetraamine, is described. An attempt has been made to explain, in terms of possible degradation reactions, the actual compounds detected in the pyrolytic breakdown.

INTRODUCTION

Many methods are available for the characterization of linear or branched polymers, but relatively few methods are available to characterize the highly crosslinked network type, such as epoxides. One method that has been developed in recent years is the pyrolysis of the polymer followed by analysis of the breakdown products by using gas chromatography.

Methods of Pyrolysis

One of the favorite methods has been the pyrolysis of the polymer on an electrically heated filament, followed by chromatographic analysis of the pyrolyzate, and early work on these lines is described by several authors.¹⁻⁵

Improved techniques of examining polymer decomposition by the filament method are described by Barlow, Lehrle, and Robb.⁶ In their work the sample was placed on a filament in the carrier gas stream, the filament was heated for 10-20 sec. and the degradation products swept directly into the chromatographic column. At lower filament temperatures there was only partial degradation of the sample, so that part of the sample remained and could be subsequently degraded by means of a pulse at a higher temperature. The polymer sample was thus subjected to an ascending stepped series of temperatures. The filament temperatures were ascertained by using substances of known melting point and thus calibrating temperature against the supply volts; above 700°C. an optical pyrometer was used. A number of thermoplastic materials were examined and some of the breakdown products characterized; in general the results supported what is otherwise known about the breakdown of these materials.

Using the filament method of pyrolysis, Szymanski, Salinas, and Kwitowski⁷ compared the methods of pyrolyzing in a vacuum, and then pumping the pyrolyzate into the chromatographic column in a second operation, with the usual method of direct entry into the column. Using a urethane sample they found the two methods gave different pictures of the breakdown. This underlines the problem in polymer degradation work that the course of degradation may well be a function, to some degree, of the method used.

The use of pyrolysis provides a convenient method of "fingerprinting" polymers for a variety of practical applications.⁸⁻¹⁰

Alternative methods of pyrolysis are the use of a small boat¹¹⁻¹³ and the injection of the sample into a heated steel chamber.^{8,14,15}

A paper by Ettore and Varadi,¹³ who favor the boat method, compares the three present methods of pyrolysis prior to chromatographic analysis.

A novel approach is described by Feuerberg and Weigel,¹⁶ who decompose much larger quantities of material (up to 1 g.) by using a special oven. Pyrolysis products were condensed in traps and introduced into the column in a separate operation.

In polymer degradation work one of the main problems is that of secondary reaction, whereby primary degradation products react either with each other or with the polymer. The low thermal conductivities of polymers also add complications as extreme temperature gradients may be set up inside polymeric materials. Diffusion problems will be important and diffusion effects will interact with secondary reactions; the problem is, therefore, highly complex.

By placing a small, approximately spherical, piece of polymer in a loop of nichrome filament ($1/8 \times 0.005$ in.) only the polymer surface is in contact with the source of heat. Because the current is only applied for a very short period there should be few small molecules attempting to diffuse from the center of the material outwards, as most decomposition will be on the surface. There is a possibility of secondary reaction during diffusion of breakdown products along the polymer-metal interface. Nevertheless, we considered these effects would be less than those encountered by using the boat or heated chamber methods.

The use of stepwise heating on the same sample raised another question, namely, that after the first heating there may be a layer of tarry material between the filament and the resin. Unless the tar had a very low thermal conductivity, which is unlikely, one cannot be sure of the temperature of the resin surface, as opposed to the temperature of the tar. If this were true, degradation of the tar need not be expected to follow the same course of degradation of the resin. If so, pyrograms would change their basic pattern with increasing temperature; in fact, this was not so, suggesting that in all cases actual resin was being pyrolyzed and not some partially degraded tarry material.

As far as the method of pyrolysis is concerned, we attempted to investigate two questions more closely: (a) the actual temperature of the filament

under working conditions; (b) the method of identifying the compounds produced during degradation.

In work up to the present time the actual identification of products has presented some difficulty. As far as chromatography is concerned, merely quoting a model compound's retention time under one set of conditions is not good enough, in our opinion. Two compounds may show the same retention times under one set of conditions whereas under other conditions this may not be the case. Thus, quoting correspondence of retention times under one set of column and temperature conditions is only a speculative identification. We have attempted a critical examination of this question, and also that of the difficulty of relating the retention times of model compounds to those of degradation products in a flowing gas stream.

The use of infrared spectroscopy or mass spectrometry on the materials emerging from the column is also possible.¹⁷ The identification of materials purely on the basis of an infrared spectrum or mass spectrometry may not itself be always very certain; moreover, mass spectrometry may not always be available.

Thermal Degradation of Epoxides

The degradation of epoxides has been studied by several methods by Neimann et al.¹⁸⁻²¹ Studies on oxidative degradation, and quasi-distillation methods of degradation *in vacuo* are described and degradation reactions proposed. Anderson²²⁻²⁴ has also investigated the question using thermogravimetry and differential thermal analysis; overall activation energies obtained by the thermogravimetric method are quoted for degradation of certain epoxides.

Two papers by Lee^{25,26} describe further the work on epoxide breakdown by use of thermogravimetry, differential thermal analysis, gas-phase chromatography, and mass spectrometry on low boiling pyrolyzates, obtained by quasi-distillation methods. The theories of Neimann and Anderson, together with Lee's explanations of the resin breakdown, are discussed in his papers. The question of the reactions involved in epoxide resin breakdown is deferred to the discussion section of this paper.

As far as the chromatographic method is concerned, very few workers divulge much detail on how the final peaks of the chromatography traces are related to known chemical compounds. It may also be considered that the use of infrared spectroscopy or mass spectrometry alone on complex mixtures of pyrolyzates may lead to varied or doubtful interpretations of the chemical nature of the breakdown products.

The effect of thermal degradation on the physical properties of epoxides is reported by Lemon.²⁷

EXPERIMENTAL

Instruments

The gas chromatograph used was a slightly modified version of a standard Perkin-Elmer Model 452. The injection block normally used in these

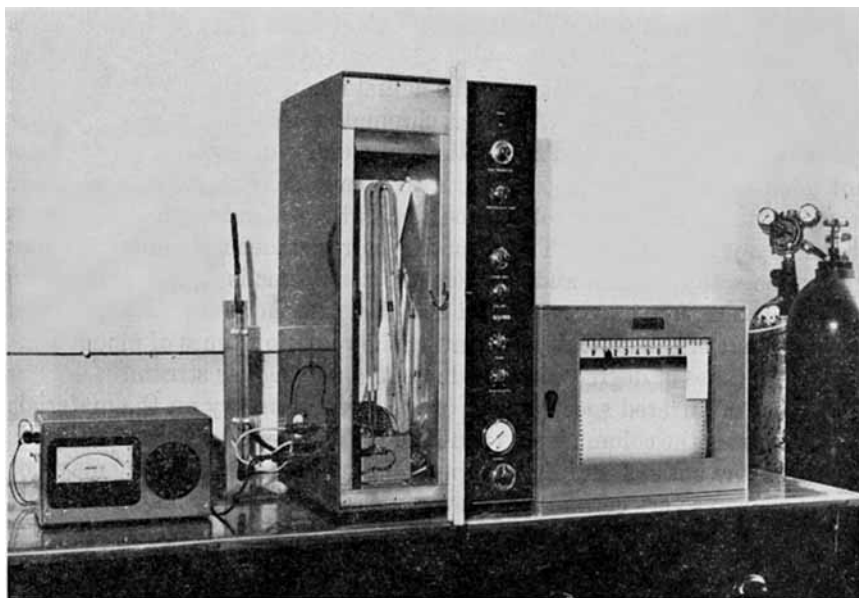


Fig. 1. Complete pyrolysis apparatus.

instruments had been removed to allow glass units of our own design to be connected to the column within the oven, thus avoiding condensation of low boiling-point materials. This was made possible by a port in the side of the instrument (Figs. 1 and 2) through which the glass units could be inserted and connected directly onto the column by means of a short piece of silicone rubber tubing. Preliminary tests had showed that this tubing did not give "noise" at the temperatures used in these experiments.

Also incorporated externally on the side of the instrument was a fast-action needle valve enabling the carrier gas to be switched on and off in a time very short compared with pyrolysis times. This meant that the carrier gas stream was diverted out of the side of the instrument's oven, through the needle valve and into the glass units where the gas would sweep any compounds produced there directly into the column.

Apart from these modifications the instrument remained unchanged. The column temperature was controlled by an oven unit capable of reaching temperatures in slight excess of 225°C . with a thermostating system capable of holding the selected temperature constant to within 0.05°C . Reproducibility of temperature could be achieved to within 0.25°C .

Two standard Perkin-Elmer columns were used. Type O column was a silicone grease on an inert dust, and type R was polypropylene glycol on an inert dust.

The instrument incorporated a standard hot wire detector operating a pen recorder in the usual way.

The carrier gas was supplied to the instrument at a pressure of approximately 25 psi. The flow rate of the carrier gas was controlled by adjusting

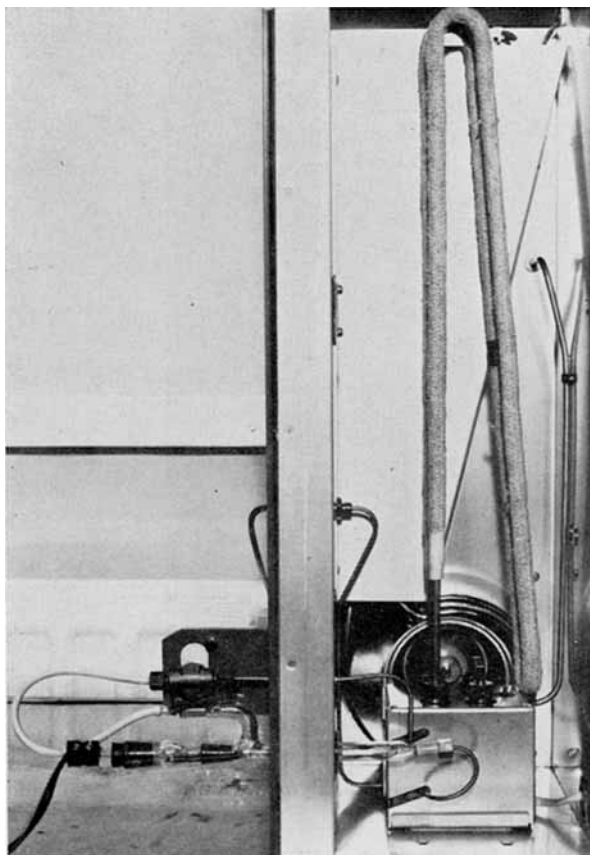


Fig. 2. Close-up showing insertion of burner in Perkin-Elmer gas chromatograph, Model 452.

the pressure regulator incorporated in the machine. This flow rate was measured by a soap-bubble flowmeter. For a given column temperature a fixed volume of gas is required to elute a specific component; increasing the gas flow will therefore shorten the time required for the component to reach the detector, but resolution may be impaired. Initial experiments showed that a flow rate of 40 ml./min. gave suitable resolution for a wide range of components and temperatures, and therefore this rate was adopted throughout.

Injection Systems

Having removed the conventional injection block, three units were built for the purpose of injecting components into the column, a pyrolyzing unit for the cured resins, a hypodermic/septum device for liquids and solutions of model compounds, and a gas buret for gases and vapors.

Pyrolysis Unit. The unit (Fig. 3) consisted of a nichrome filament, previously rolled to a flat cross-section of $1/8$ in., welded in the form of a loop



Fig. 3. Pyrolysis unit.

between two rigid nichrome rods. The two rods led out of a glass container via rubber bungs and were connected into an electrical circuit (Fig. 1). The rubber bungs gave no "noise." On passing a current through the system the filament acted as a resistance heater and pyrolyzed samples previously mounted in the loop. To obtain the temperature of the filament, a small thermocouple of 0.004-in. chrome/amel wires was spot-welded onto the middle point of the filament loop and by this means the temperature of the filament was directly correlated with the current supplied to it for any set of gas and oven conditions. The filament unit mounted in its glass container was connected to the gas chromatogram so that the carrier gas would sweep past the filament. The carrier gas would take with it any vapors or gases resulting from pyrolysis into the column where separation would take place. As a check on the accuracy of the thermocouple and bridge several compounds of known melting point, such as diphenyl urea, and sodium chloride were placed on the filament. The temperature, as recorded by the thermocouple, corresponded to those melting points to within $\pm 5^{\circ}\text{C}$.

It was clear that the temperature of the wire would be affected by the flow of gas and by the oven temperature of the instrument; thus, several calibrations of temperature against current in the filament were undertaken to account for burning under flowing gas conditions (dynamic con-

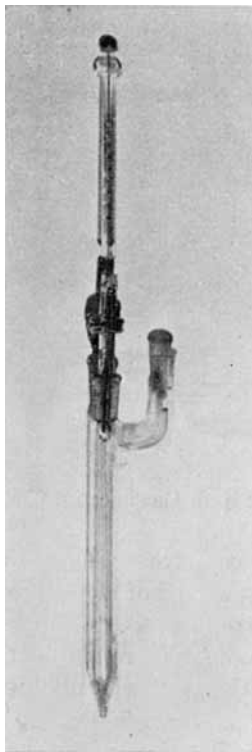


Fig. 4. Hypodermic injection unit.

ditions) and stationary gas conditions (static conditions). It was hoped by these means to obtain true filament temperatures.

Because all the above experiments were performed on uncoated wire it was considered a coating of resin might alter the temperature of the wire, due to thermal insulation. The filament was thus coated with unhardened resin MY750 and tested, under static conditions, in the normal pyrolyzing position in the apparatus. Temperatures, as measured by the attached thermocouple, still corresponded to the voltage calibration data, thus suggesting that no effective thermal insulation had occurred. Later on, solid polymer was placed in the fold of the loop, secured by fine wire, and the question of thermal insulation was not so pertinent. After all checks and calibrations were performed, the current was normally taken as indicative of temperature, using calibration charts.

Hypodermic Injection Unit. Liquids and solutions of compounds were injected into the gas stream of the chromatogram by means of a microliter hypodermic syringe piercing a rubber septum mounted into a glass unit (Fig. 4). The liquid, entering the heated glass tube inside the instrument oven, evaporated, and the vapors entered the column in the usual way.

Gas Injection Unit. Model gases (produced by a variety of reactions, e.g., Grignard compounds and water), were generated into the gas buret

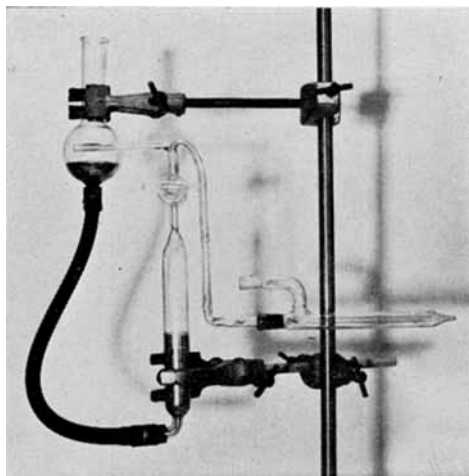


Fig. 5. Gas injection unit.

(Fig. 5), through a two-way valve. The gas could then be fed into the chromatograph by allowing a head of mercury to displace a known volume of gas into the carrier gas stream at a controlled rate. The efficiency of this system was assessed by comparing retention times of ether liquid (using standard conditions) and ether vapor by using the gas buret. Close agreement was obtained.

Carrier Gas

Preliminary experiments with helium and nitrogen showed that, because of its high thermal conductivity, helium led to greater sensitivity than nitrogen but had the disadvantage of cooling the pyrolyzing filament to such a degree that high pyrolyzing temperatures were difficult to achieve. It was for practical reasons, therefore, that white spot nitrogen was chosen as the carrier gas and was used throughout the main experiments. However, by using nitrogen as a carrier, it may be noted that any nitrogen produced during pyrolysis would not be detected and that air would be recorded as only oxygen.

The specification of white spot nitrogen is a maximum 500 ppm impurity

Methods and Procedure

Pyrolysis of Materials. To pyrolyze unhardened liquid resins or liquid amine curing agents the burner filament was dipped into the substance and the excess fluid allowed to drain off, while for solid and hardened resins a small particle of the material (0.01–0.02 g.) was carefully wired onto the loop of the filament. The burner filament was then inserted into its glass container which in turn was connected to the column of the gas chromatogram.

To pyrolyze a substance at a specific temperature a predetermined current was passed through the filament. The products of pyrolysis were

then passed through the column resulting in a peak (or peaks) being plotted on the recorder. Temperatures were raised, for the same specimen of polymer, according to a stepwise sequence.

Model Compounds. Model or known compounds were introduced into the column in small quantities by the use of the hypodermic system or the gas buret system. It was noted that when certain liquid models were injected into a flowing or dynamic gas stream their retention times varied with the amount used. This was found to be due to a finite evaporation time not normally encountered with the use of the conventional injection-block system, where evaporation is considered to be instantaneous. It was also found that the gas buret could not be used with a flowing gas stream, because the carrier gas pressure was far in excess of the buret pressure resulting in the model gas being forced back into the buret.

Standardized Method of Introducing Compounds into Column. To overcome the above mentioned practical difficulties the following method was devised. The flow of carrier gas was turned off at the snap-action valve and after a pause of 10 sec., to allow the carrier gas pressure to fall, the compound was injected either by hypodermic syringe or by gas buret. This was followed by a further pause of 30 sec. to allow for evaporation (found by experiment to be the optimum time), after which the carrier gas was switched on and the retention times of substances timed from that moment. In order that the pyrolysis of materials should conform as closely as possible to the above conditions, the following procedure was adopted. A pause of 10 sec. after switching the gas off was followed by a period of burning. This was followed by a further pause, timed to give an overall total of 40 sec., (e.g., 10 sec. pause, 5 sec. burning period, 25 sec. pause) before switching on the gas. Retention times were estimated from the moment of turning on the gas. The burning time was achieved by a switch and stop watch.

To check the accuracy of this method of introduction, ether was used in all three units as a vapor or a liquid and was found to have identical retention times for all three, regardless of quantity.

EXPERIMENTAL RESULTS

The materials chosen for pyrolysis were supplied by CIBA (A.R.L.) Ltd. and were standard commercial products. The epoxide system used was based on Araldite MY750 resin cured with an amine hardener, Araldite HY951. The formulation used was 100 parts by weight MY750 to 10 parts HY951; these two components were thoroughly mixed together and cured for 12 hr. at 50°C. to ensure a fully crosslinked polymer.

The resulting polymer was then degraded by pyrolysis under a variety of conditions (Table I) and the products analyzed in the gas chromatograph. The peaks resulting from these products were recorded and the retention time of the major ones noted and compared with retention times of models.

Also pyrolyzed for purposes of comparison were unhardened MY750, HY951, and MY750 hardened with 1,2-diaminoethane.

TABLE I
Pyrolyzing Conditions for the Degradation of MY750/HY951^a

| Column designation | Oven temperature, °C. | Pyrolyzing temperature, °C. | Pyrolyzing time, sec. |
|--------------------|--------------------------|-----------------------------|-----------------------|
| 0 | 200 | 400 | 5 |
| | | 500 | 5 |
| | | 600 | 5 |
| | | 700 | 5 |
| | | 800 | 5 |
| | | 800 | 10 |
| 0 | 150 | 350 | 5 |
| | | 450 | 5 |
| | | 550 | 5 |
| | | 650 | 5 |
| | | 750 | 5 |
| | | 750 | 10 |
| 0 | 100 | 200 | 5 |
| | | 300 | 5 |
| | | 400 | 5 |
| | | 500 | 5 |
| | | 600 | 5 |
| | | 700 | 5 |
| | | 700 | 10 |
| | | 700 | 10 |
| 0 | 50 | 700 | 5 |
| | | 700 | 10 |
| R | Series repeated as above | | |

^a Range setting 1; detector supply setting 2.

HY951 is substantially triethylenetetraamine; resin MY750 is substantially the diglycidyl ether of bisphenol-A having an average epoxy content of 5.2 eq./kg.

General Observations

The following are some general observations made on the traces produced by the degradation products of the pyrolysis of MY750/HY951 under the conditions stated in Table I.

(1) Using either column at any given oven temperature there is a marked increase in peak heights recorded once the pyrolyzing temperature is in excess of 450–500°C. An example of this is given in Figure 6. Below 400°C. relatively small amounts of materials are evolved.

(2) On increasing the pyrolyzing temperatures above 500°C. the patterns and retention times of the peaks do not alter but the peak heights do increase, thus showing that larger amounts of the same components are given off at the higher temperatures (see Fig. 6).

(3) More peaks (or components) are obtained at high oven temperatures. This may be explained by high boiling point materials condensing and not passing through the column at low oven temperatures (Figs. 7–10).

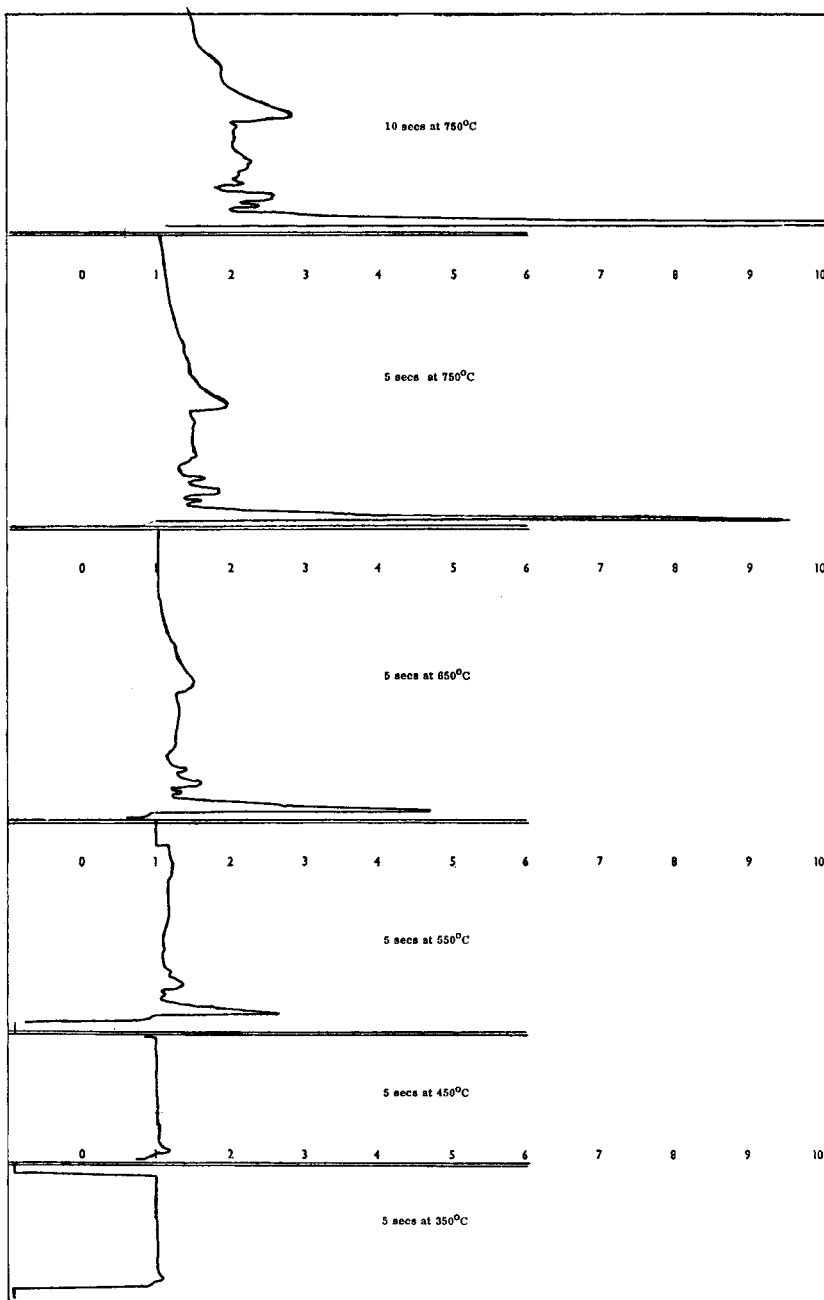


Fig. 6. Oven temperature 150°C.; column type 0; MY750/HY951.

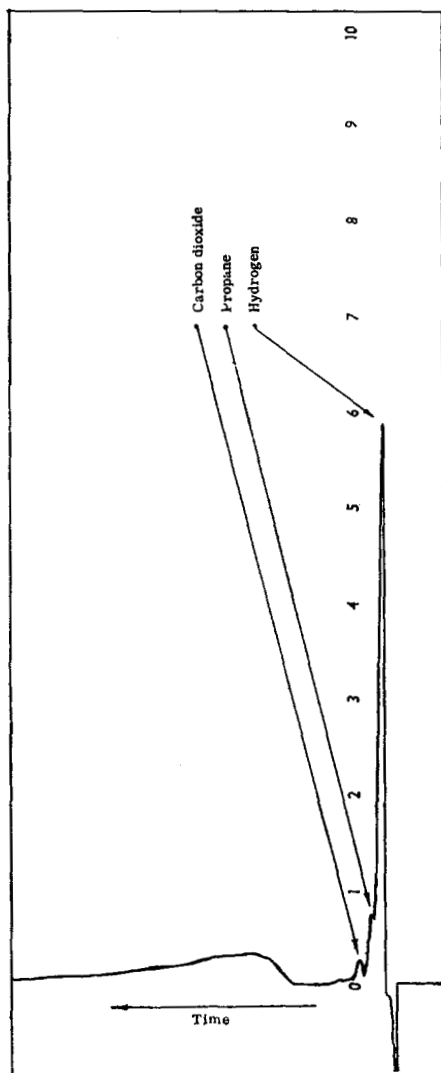
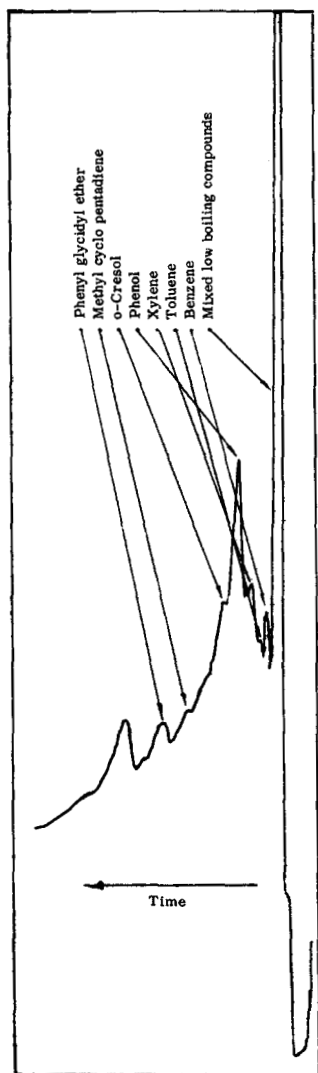


Fig. 7 (Top). Oven temperature 200°C.; column type 0; MY750/951 pyrolyzed for 10 sec. at 800°C.
Fig. 8 (Bottom). Oven temperature 100°C.; column type 0; MY750/HY951 pyrolyzed for 5 sec. at 700°C.

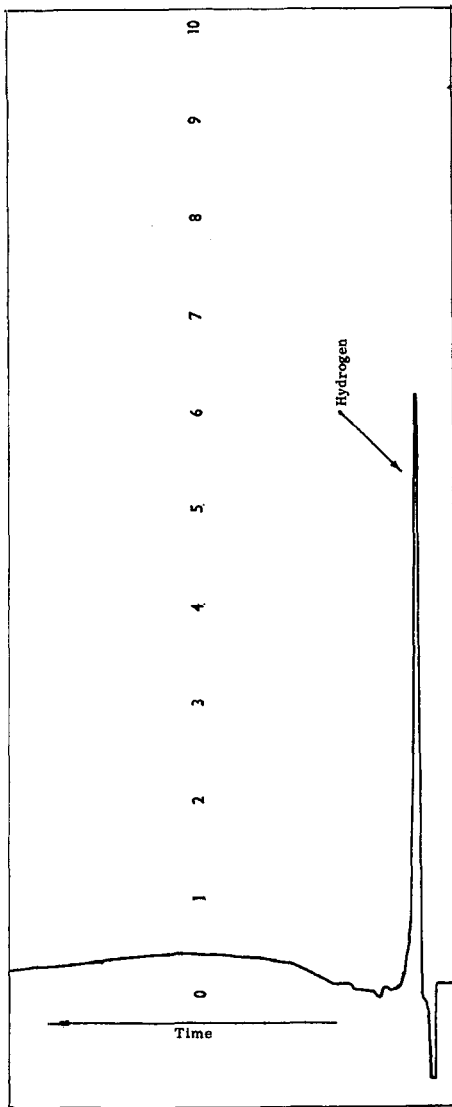
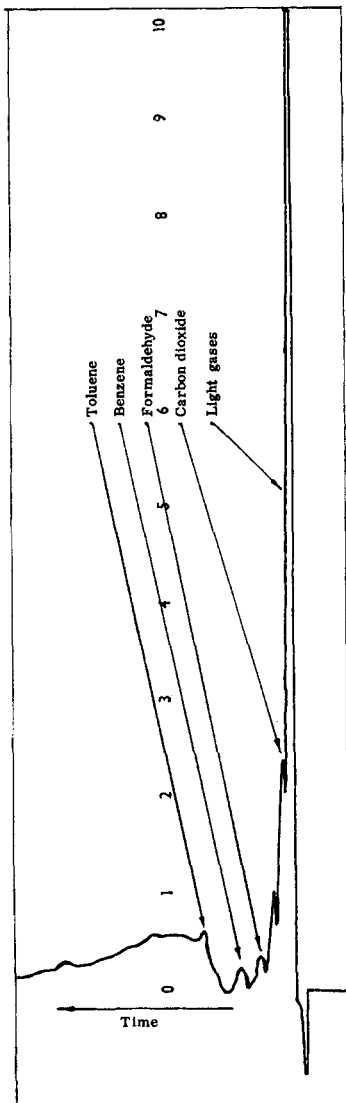


Fig. 9 (Top). Oven temperature 150°C.; column type R; MY730/HY951 pyrolyzed for 5 sec. at 750°C.
 Fig. 10 (Bottom). Oven temperature 50°C.; column type R; MY750/HY951 pyrolyzed for 10 sec. at 700°C.

(4) After pyrolyzing either hardened or unhardened resins there always remained behind on the burner a relatively large amount of carbonaceous material.

(5) The breakdown pattern with the use as hardener of 1,2-diaminoethane was similar to the above.

Use of Model Compounds

Having recorded and timed the major peaks for the pyrolyzed resin under a variety of conditions (Table I), model compounds of suspected breakdown products were introduced into the columns by the methods stated. If the retention time of a model compound corresponded with that of a major peak in the breakdown products, then the model would be tried under a variety of oven temperature conditions and columns identical to those used for the degradation of polymer. If the model's retention time always corresponded to the unknown peak under all practical conditions it was assumed that the unknown peak was produced by the same chemical as the model, and the model compound was listed as a highly probable breakdown product.

Certain model compounds could not, however, be tested under a wide variety of conditions (e.g., phenyl glycidyl ether, because of its high boiling

TABLE II
Compounds Detected in the Pyrolysis of MY750/HY951

| Compound | |
|-----------------------|-----------------|
| Hydrogen | Highly probable |
| Carbon dioxide | " |
| Benzene | " |
| Toluene | " |
| Phenol | " |
| Mixed xylenes | " |
| Mixed cresols | " |
| Formaldehyde | Probable |
| Acetaldehyde | " |
| Phenyl glycidyl ether | " |
| Carbon monoxide | Speculative |
| Methane | " |
| Propane | " |
| Acetone | " |
| Methylcyclopentadiene | " |
| 2-Isopropyl phenol | " |
| Ammonia | Undetected |
| Ether | " |
| Methyl ethyl ketone | " |
| Anisole | " |
| Phenetole | " |
| Piperazine | " |
| Bisphenol-A | " |
| HY951 (used as model) | " |

point, only produced a peak when passed through a column running at an oven temperature of 200°C.). Therefore, this retention time could only be matched against pyrolysis products that had been passed through a column at the same high oven temperature. Such compounds thus identified were listed as probable, and could only be checked over a narrow range of conditions.

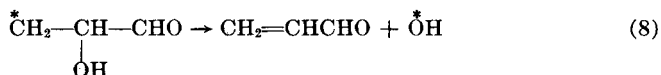
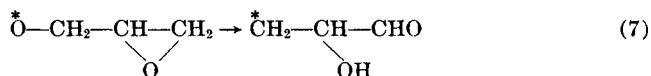
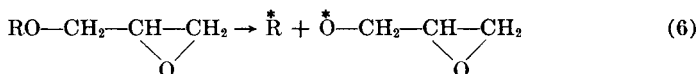
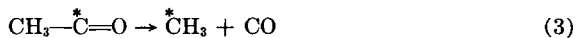
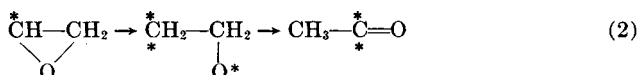
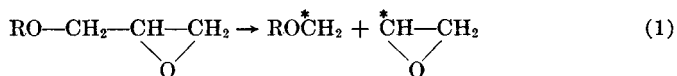
Model compounds found to correspond to an unknown peak only under one set of conditions were termed speculative.

Model compounds of suspected breakdown products that were tested and found not to correspond with any given peak produced by pyrolysis were said to be undetected and listed as such. A full list appears as Table II, but no such distinction has been made between compounds in labeling, e.g., Figs. 7-10.

DISCUSSION

There are two main theories of thermal epoxide degradation: that due to Neimann et al.²¹ and that due to Lee.^{25, 26}

As a result of studies based on quasi-distillation methods, including the use of tagged carbon atoms, Neimann proposed the degradation reactions shown in eqs. (1-8).



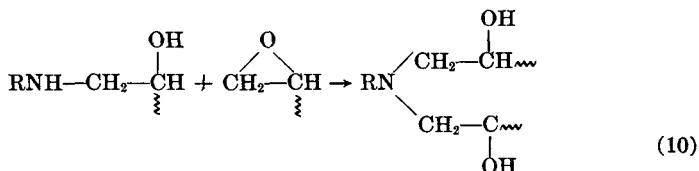
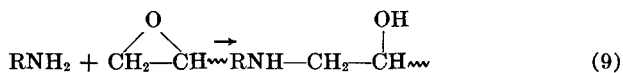
According to this view, acetaldehyde, formaldehyde, and acrolein will be principal degradation products. Neimann's theory would explain the presence of aldehydes, such as formaldehyde, acetaldehyde, and acrolein; these are not, however, according to our analysis, the major decomposition products, although the presence of formaldehyde is probable. Our evi-

dence thus leads us to agree with Lee that Neimann's scheme does not go far in explaining the presence of many of the compounds identified.

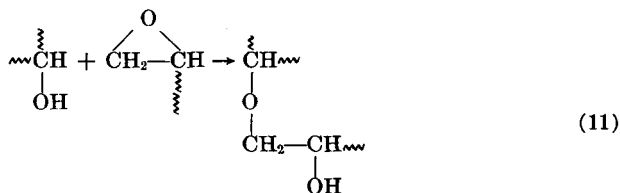
The schemes put forward by Lee merit detailed discussion.

Scheme 1. Here Lee follows Anderson in postulating the isomerization of residual epoxide groups to give several aldehydes. Of these we believe formaldehyde to be a probable decomposition product, but the small quantities suggest, certainly in the cured resin, that this is a secondary reaction. This would be expected. Lee's other schemes all depend on an initial attack on the ether groups.

Scheme 2. Scheme 2 is also based on the attack on ether groups formed from the polymerization of epoxide groups to form ethers. Several forms of cleavage of these ethers are described as giving rise to carbon monoxide, vinyl phenol, acrolein, ethylene, and allyl phenols and isopropenyl phenols. He also predicts allene, and its dimerization and cyclization product, methylcyclopentadiene. In work of this kind it would be rash to deny categorically the presence of these materials amongst the decomposition products; in our opinion, of these only carbon monoxide is an important breakdown product. In materials cured by primary and secondary amine hardeners the most important reactions are those given in eqs. (9) and (10):



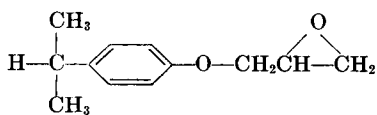
and reactions of hydroxyls, so formed, with epoxides are as given in eq. (11):



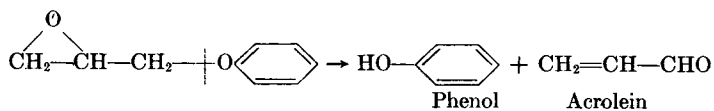
The third reaction, eq. (11), will yield ether links, but there is evidence to suggest that this third reaction hardly proceeds at all in the presence of primary and secondary amines.²⁸ Reaction of epoxide groups with epoxide groups is in competition with the reaction of epoxide and amine groups, and one would suppose that this reaction also would not proceed to any great extent. There are, of course, ether groups already existing, and these may break down in ways similar to those suggested by Lee.

In Scheme 3 Lee suggests that residual epoxide groups will form 1,2,3-triethers and claims that this is the most predominant species in the cured

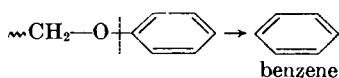
There would also be molecules such as II:



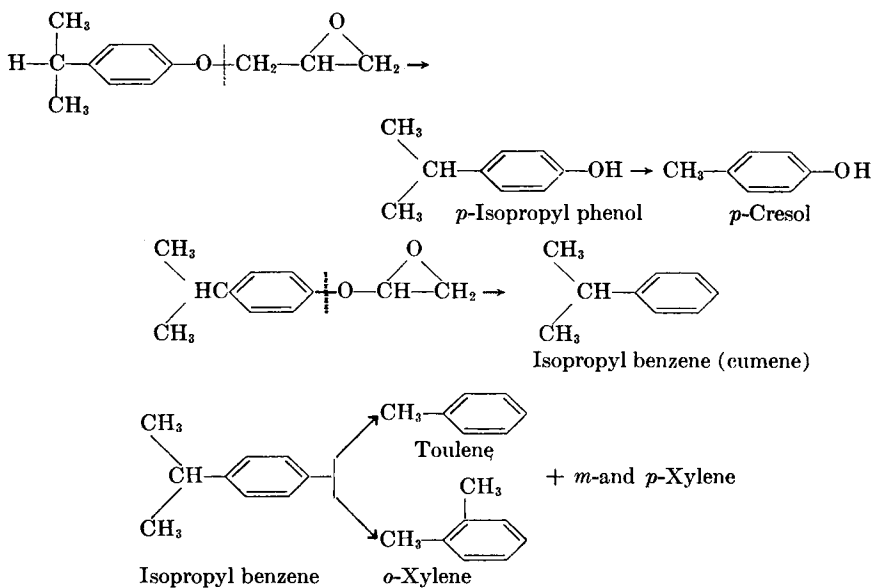
Further scission at the ether group may now occur to (I) thus:



or



Decomposition of (II) may follow similar lines:



The above reactions may be supposed to proceed by free radical mechanisms.

(3) The reactions of Lee and Anderson may be accepted as explaining carbon monoxide, and probably the dioxide, and also the various aldehydic products and the speculative presence of methylenecyclopentadiene.

The above revised degradation schemes appear to explain most of the compounds identified in the breakdown reaction. The most outstanding difficulty is the absence of nitrogen compounds that could have been derived from the aliphatic amine hardener, triethylenetetramine.

CONCLUSIONS

All the materials identified from the decomposition of epoxides appear to come from the main skeletal structure of the resin, so that the most difficult problem yet outstanding is the question of what happens to the amine hardeners on pyrolysis. The only fact that we can be sure of is that they are not regenerated as such by any simple reversible mechanism. It is also known that the nitrogen does not appear as ammonia or piperazine.

At present one would expect that changing the resin structure will produce a markedly changed series of breakdown products whereas different amine hardeners should not. Some of Lee's results support this hypothesis, but much amplification is needed.

It may well be worth while investigating the tarry residues deposited on the glass wall of the pyrolysis tube. These may be dissolved in a suitable solvent and infrared analysis may at least reveal the presence of nitrogen functions.

The authors would like to thank Professor A. J. Kennedy for his continued support of the work and Dr. R. S. Lehrle (Birmingham University) for several very helpful conversations. The authors would also like to thank Dr. A. J. Duke, formerly of CIBA (ARL) Ltd., for several helpful suggestions, and CIBA (ARL) Ltd. for the samples of material with which this work was done.

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Résumé

On décrit l'utilisation de la chromatographie en phase gazeuse pour l'examen de la dégradation pyrolytique de résines époxydées. La méthode est basée sur la pyrolyse du matériau au moyen d'un filament chauffé électriquement; les difficultés de la méthode sont examinées et les essais effectués en vue de les éviter sont décrits. On décrit la dégradation pyrolytique d'une résine à base d'éther glycidique de bis-phénol-A durcie au moyen d'éthylène-diamine et également au moyen de triéthylène-tétramine. On essaie d'expliquer, sur la base de réactions de dégradation possible, les composés mis en évidence au cours de la pyrolyse.

Zusammenfassung

In der vorliegenden Arbeit wird die Verwendung der Gaschromatographie zur Untersuchung des pyrolytischen Abbaus von Epoxydharzen verwendet. Die Pyrolyse des Materials wird mittels eines elektrisch geheizten Fadens durchgeführt; die Schwierigkeiten des Verfahrens werden überprüft und Versuche zu ihrer Überwindung beschrieben. Der pyrolytische Abbau eines Harzes auf Basis des Glycidiläthers von Bisphenol-A, gehärtet mit 1,2-Diaminoäthan und auch Triäthylentetramin wird beschrieben. Es wurde versucht, an Hand der möglichen Abbaureaktionen das Auftreten der tatsächlich bei der Pyrolyse gefundenen Verbindungen zu erklären.

Received May 14, 1965