

## Further Aspects of the Thermal Degradation of Epoxide Resins

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### Synopsis

This paper describes an investigation into the degradation of a purified epoxide based on the diglycidyl ether of bisphenol A hardened with *p,p'*-diaminodiphenylmethane. The method used was that of hot-wire pyrolysis followed by gas chromatography. Special attention was given to the problem of solid residues formed on the pyrolyzer tube, and evidence was found that these probably contain oligomers. Resonance-stabilized free radicals also appear to be formed, and evidence is found to support the idea of dehydration during degradation, originally put forward by Lee. An attempt, based on first principles, is made to explain the degradation of epoxides, using evidence from previous work as well as that described in this paper.

### INTRODUCTION

There is an increasing interest in the pyrolysis of polymers, followed by gas chromatographic analysis, the general topic of polymer pyrolysis is reviewed by Dandoy.<sup>1</sup> The method of hot-wire pyrolysis followed by gas chromatography, as applied to epoxy resins, is described by Lee<sup>2</sup> and Stuart and Smith.<sup>3</sup> A variety of other analytical methods have been used to investigate the thermal degradation of epoxides. Anderson<sup>4-6</sup> has described the use of DTA and TGA with epoxides. Lee<sup>2,7</sup> has described the application of DTA, TGA, gas chromatography, quasi-distillation methods, and mass spectrometry to this problem. He discusses mechanisms of degradation which will be referred to in the appropriate section of this paper. Neimann, Kovarskaya, et al.<sup>8-13</sup> have made investigations using quasi-distillation methods, mass spectrometry, ESR, and radioactive tagged carbon methods. Various degradation mechanisms suggested by these workers are discussed by Lee and will be referred to later in this paper.

The thermal degradation of epoxides investigated by quasi-distillation techniques is also reported by Madorsky and Strauss<sup>14</sup> and by Coleman.<sup>15</sup>

Special attention to the oxidative degradation of epoxide resins is described by Park and Blount<sup>16</sup> and also Dante and Conley.<sup>17</sup>

Changes in both mechanical and electrical properties caused by thermal degradation of epoxides are described by Lemon<sup>18</sup> and Jacobi and André.<sup>19</sup>

The amount of previous work on hot-wire pyrolysis of epoxides has not been considerable, and we attempt to extend the method in this paper to the

study of the degradation of an epoxide resin cured with *p,p'*-diaminodiphenylmethane. The resin was in fact a purified form of the diglycidyl ether of bisphenol A. Special attention has been given to the analysis of the solid residues left on the pyrolysis tube. By means of purified materials and close control of conditions such as temperature, it was hoped to obtain an idealized picture of the degradation of epoxides. The much more complex phenomena of degradation under realistic conditions, is better deferred, in our opinion, until some idea of the fundamental mechanism has been obtained.

## EXPERIMENTAL AND RESULTS

### Materials

Materials for degradation studies were supplied by C.I.B.A. (ARL) Ltd. and consisted of the diglycidyl ether of bisphenol A and *p,p'*-diaminodiphenylmethane (DDM). The diglycidyl ether of bisphenol A was supplied as substantially pure compound, without further polymerization, and was recrystallized from ethanol to constant melting point (42°C.). DDM was recrystallized from water and vacuum dried over phosphorus pentoxide to a melting point of 91°C. (lit. m.p.:<sup>20</sup> 93°C.).

ANAL. Calcd. for diglycidyl ether of bisphenol A: C, 74.1%; H, 7.1%. Found: C, 73.9%; H, 7.0%; Cl, 0.23%.

A small amount of chlorine impurity was noted.

ANAL. Calcd. for DDM: C, 78.7%; H, 7.1%; N, 14.1%. Found: C, 78.5%; H, 7.0%; N, 14.5%.

The raw materials used were thus substantially pure.

### Methods of Cure

Purified resin A and hardener were mixed in the ratio of 100 parts resin to 27 parts hardener (DDM) by weight. This was done at 100°C. until a homogeneous mixture was formed. This was cooled and placed in a vacuum desiccator for 3 hr. for degassing. The material was poured in a polyethylene mold to produce a film of approximately 1 mm. thickness. The mold was secured and oven-cured to the following schedule: 16 hr. at 55°C., followed by 2 hr. at 125°C., followed by 2 hr. at 175°C. The polyethylene mold was left around the epoxide for the full cure schedule; at higher temperatures it melted round the epoxide disk forming a protective coating and preventing surface oxidation. Air-curing of epoxide disks produced surface browning around 175°C. The polyethylene mold largely prevented this and released easily at the end of the curing process, after cooling.

Resin B was treated in a similar way, except that the mold was removed for cure above 125°C. The heating schedule was modified also to 2 hr. at 125°C., followed by 1/2 hr. at 200°C. A very dark brown surface was noted in disks produced by this method.

Resin C was cured exactly as resin A, except that the polyethylene mold was removed for the post-cure. However, pyrograms and infrared spectra of all three resins were identical, thus the differing cure methods did not give major differences in the finished products.

In addition to preparing disks for subsequent pyrolysis, attempts were made to follow the curing process by using a Perkin-Elmer infrared spectrometer, Model 21. A mixture of resin and hardener (100:27 by weight) was prepared at 100°C. and cooled to room temperature. All the functional groups could be identified by infrared spectroscopy, as for the separate materials.

The mixtures were examined in two ways: (a) as thin films (0.002 in. thick), subjected to the cure schedules of resins A, B, and C, being examined at intervals during the process; (b) pressed between two KBr disks and heated to 100°C. in the beam of the spectrophotometer by means of hot air directed on the disk. Continuous spectra were run to observe changes in infrared absorptions during cure.

As a check on both processes, spectra on a number of model compounds containing the structures contained in the resin and hardener were also observed.

The two techniques produced the same overall picture. Primary amine and epoxy absorptions either disappeared or weakened, whereas absorption due to secondary alcohols increased. The important point was that a number of variations in cure schedule produced no important differences in the infrared spectra at temperatures up to and including 175°C.

However, it was found that at 225°C. air-curing produced very definite absorptions at 1725 and 1665  $\text{cm.}^{-1}$ , if continued for  $\frac{1}{2}$  hr. This was on films of 0.002 in. thickness. Thicker films did not give good transmittance spectra. A second experiment, at 200°C., curing for  $\frac{1}{2}$  hr., showed the development of the same peaks, whereas larger samples of resin B finally cured at the same temperature, for the same time, did not. This suggests a surface effect due to oxidation and the formation of carbonyl groups, which checks with the work of Conley.<sup>21</sup>

From this it was supposed that resins A and B, later pyrolyzed, had not been subjected to oxidation to any considerable degree during their cure schedules. Care was taken in purification of raw materials and in the subsequent cure to ensure that the materials being examined were a reasonable approximation to the ideal crosslinked epoxy-resin structure.

### Pyrolysis Methods

The method of pyrolysis used and the gas chromatographic analysis of the pyrolysis products was very similar to that already described by Stuart and Smith.<sup>3</sup>

Briefly, this consists of a heated, looped nichrome filament to which resin is attached, placed in a glass pyrolyzer tube directly in the stream of gas entering the gas chromatography column. The tube is mounted inside the oven of a Perkin-Elmer Model 452 gas chromatograph, which ensures that

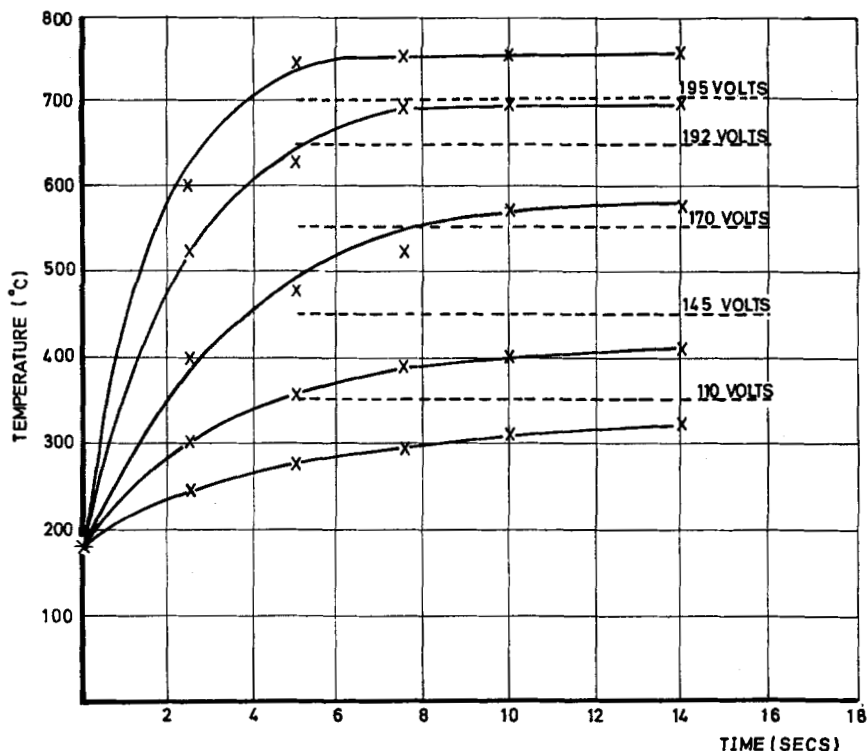


Fig. 1. Temperature vs. time; oven temperature 185°C.

only materials with boiling points greater than the oven temperature will condense on the walls of the pyrolysis tube. Lower-boiling point fragments enter the gas chromatography column and are separated in the usual way. Up to the present time we have attempted to identify the compounds separated by gas chromatography by comparison of their retention times with those of model compounds. In previous work the tarry residues found on the wall of the pyrolyzer tube were not investigated.

**Filament Temperature Calibrations.** It was decided to examine the question of filament temperature more closely than previously, and all pyrolyses were performed with a chromel-alumel thermocouple spot-welded onto the middle point of the filament. The nichrome filament was so shaped that a 2-4 mg. sample of cured resin could be inserted into it and a steel wire staple was fitted behind the sample in order to wedge it in place and prevent the sample sliding out of place at the beginning of pyrolysis. The filament was calibrated with the wire staple in place, both with and without resin. A new resin sample was used for each pyrogram.

Curves showing the variation of temperature with time were plotted for oven temperatures of 140 and 185°C., an example is shown in Figure 1. These curves all suggested that 10 sec. represented a minimum pyrolysis time. If material (2-4 mg.) was placed in the filament there appeared to be

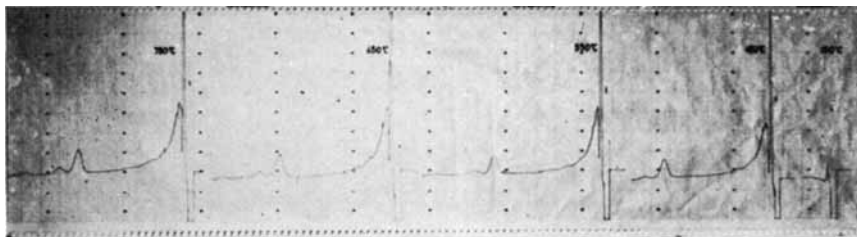


Fig. 2. Pyrograms at 100°C. intervals; oven temperature 140°C.

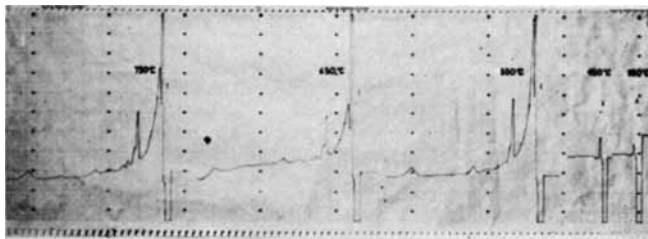


Fig. 3. Pyrograms at 100°C. intervals; oven temperature 185°C.

a small insulation effect, and this was allowed for in calculating filament temperatures. Having ascertained true filament temperatures as far as was possible, materials were pyrolyzed according to the stepwise sequence described first by Barlow et al.<sup>22</sup> and subsequently by Stuart and Smith.<sup>3</sup>

**Pyrograms and Retention Times.** Attempts were made to identify breakdown products using the stepwise filament heating process and inserting a fresh piece of resin for each burn up. White spot nitrogen was used as carrier gas and a column using trixylenyl phosphate was employed (maximum temperature 190°C.). Oven temperatures used were 140 and 185°C.

To ensure reproducible pyrograms the following conditions were observed: (a) standard cure procedures on purified materials; (b) sample size of 2–4 mg.; (c) rigorous exclusion of air from the pyrolysis tube before pyrolysis by flushing with nitrogen for 20 min.; (d) cleaning of wire with acetone and fresh samples for each pyrolysis experiment; (e) a pyrolysis time of 10 sec.

Procedures for pyrolysis of the sample were the same as those described by Stuart and Smith.<sup>3</sup> The method of static pyrolysis involved turning off the carrier gas for 15 sec., pyrolysis for 10 sec., allowing the pyrolyzate 30 sec. to attain oven temperature and then turning on the carrier gas. Retention times were measured from this instantly by means of a stop-watch.

Pyrograms were produced at 100°C. intervals from 350 to 750°C. at oven temperatures of 140 and 185°C. (Figs. 2 and 3). It is clear that the same pattern of peaks is being repeated at the higher temperatures of pyrolysis, but with the trixylenyl phosphate column, resolution of the different pyrolysis products is inferior to that previously observed with silicone gum and polypropylene glycol columns.<sup>3</sup> Successive runs showed scatter in the re-

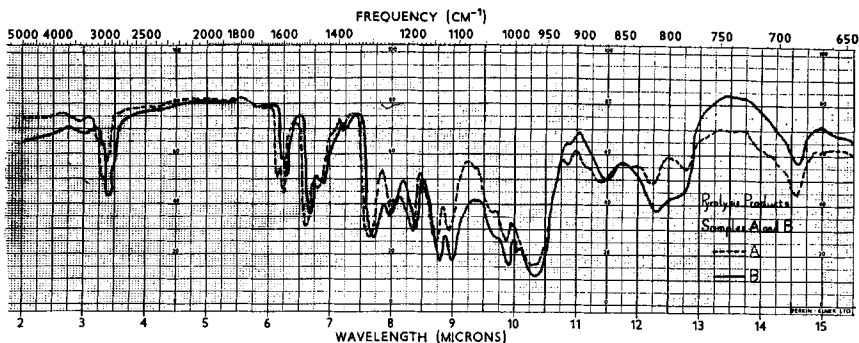


Fig. 4. Infrared spectra of pyrolysis products from (---) samples A and (—) sample B.

tention times that made identification of the peaks uncertain. Model compounds were injected as previously described<sup>3</sup> by use of the static procedure. With samples of 1  $\mu$ l. or less, retention time was independent of sample size. In our opinion this column was relatively easily overloaded; varying quantities of pyrolyzate may have accounted for scatter in retention times of the pyrolyzates.

The relative ease of overload and inferior resolution suggested that this column is not as satisfactory as those previously used for this type of work.

Resins A, B, and C gave identical pyrograms, suggesting there was no great difference in degradation behavior caused by their different cure treatment. Weight loss experiments on the glass pyrolyzer unit were conducted with resin C and showed that the proportion of material which was swept through the column was less than 20%. This implied that only a small fraction of the sample was being decomposed into very volatile materials; this was presumably the part of the resin sample nearest to the hot filament. The rest was decomposed into fragments which condensed around the inside of the pyrolysis tube and which were later investigated.

In all pyrograms there appeared to be no complete pyrolysis below 450°C. as far as the method of detection could determine.

**Examination of Products Collected from the GLC Column.** Although the columns used in the gas chromatography were analytical, it was found possible to trap materials emerging from the column. Some materials condensed in the Teflon exit tube at room temperature and were extracted with acetone, other materials emerging from the column were collected on a cold finger (acetone-ice) and subsequently removed by washing with acetone.

Samples collected for analysis are summarized as follows: sample A—resin A, oven temperature 185 and 140°C. (mixture); sample B—resin C, oven temperature 185°C. (all products combined except the last); sample C—resin C, oven temperature 185°C. (last product); sample D—resin A, oven temperature 140°C. (material from cold finger).

A portion of each of the acetone solutions from the four samples detailed above was dried over anhydrous copper sulfate (16 hr.), filtered, and solvent

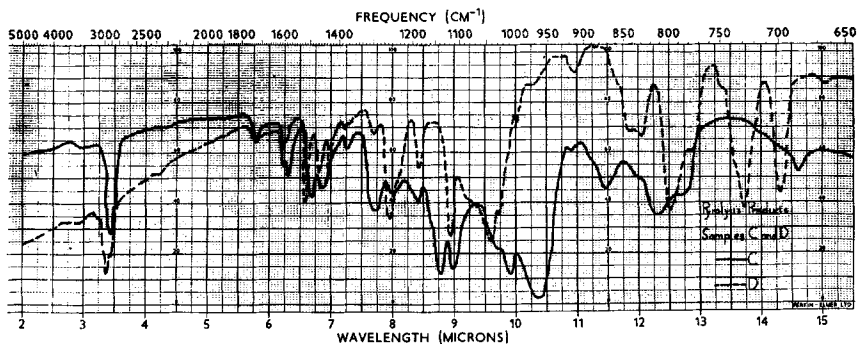


Fig. 5. Infrared spectra of pyrolysis products from (---) sample C and (—) sample D.

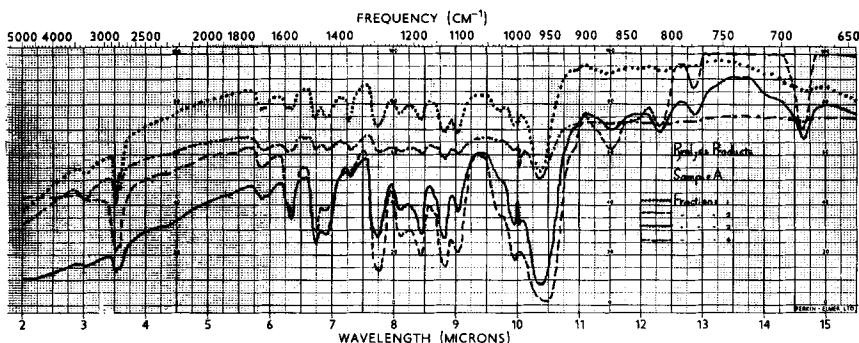


Fig. 6. Infrared spectra of thin-layer chromatographic fractions of sample A: (···) fraction 1; (---) fraction 2; (—) fraction 3; (-·-) fraction 4.

evaporated off. After drying, an infrared spectrum was taken of each sample, using either the KCl disk method or smears between rock salt windows (Figs. 4 and 5). Sample A containing products from the pyrolysis of resin A was treated by thin-layer chromatography (absorbent phase aluminum oxide HF254; eluants *n*-hexane, chloroform, and acetic acid in ratio 6:3:1). Determination of separated fractions was done by inspection of the slide in visible and ultraviolet light, and also by the use of a ninhydrin spray reagent.

The fractions were separated by scraping off the appropriate zones, extracting with acetone, filtering, drying (anhydrous copper sulfate), refiltering, and removal of solvent. KBr disks were made up for each fraction, and infrared spectra were run on each separated zone (Fig. 6).

On larger amounts of sample A, Lassaigne and Liebig sodium fusion tests were performed.

On examining the infrared spectra of samples A, B, C, and D it was noted that A, B, and C were similar to a great extent, whereas the spectrum of sample D resembled one of the solid residue spectra.

General points noted in spectra A, B, and C were: (a) aromatic C=C absorptions in the 1600 and 1450 cm.<sup>-1</sup> regions were present; (b) secondary

hydroxyl absorptions at 3500 and 1100  $\text{cm.}^{-1}$  were missing; (c) aryl ether peak at 1250  $\text{cm.}^{-1}$  had receded in importance; (d) a new peak, believed to be *trans* C=C, had appeared at 1630  $\text{cm.}^{-1}$ ; (e) a peak at 1310  $\text{cm.}^{-1}$ , due to secondary amine, had increased; (f) a strong peak, probably due to *trans* C=C, appeared at 970  $\text{cm.}^{-1}$ .

In addition to this, alkane absorptions around 3000  $\text{cm.}^{-1}$  were the same as in the cured compound, and the C—CH<sub>3</sub> peaks were present at 1460 and 1390  $\text{cm.}^{-1}$ . The C(CH<sub>3</sub>)<sub>2</sub> peaks were all present at 1150, 1130, and 780  $\text{cm.}^{-1}$ . A peak for 1,4 substitution appeared at 820  $\text{cm.}^{-1}$  and also at 1045  $\text{cm.}^{-1}$ , while one for C—Cl at 690  $\text{cm.}^{-1}$  was also noted.

The thin layer chromatograph work on sample A indicated four fractions. In ultraviolet light the top band was light blue and the second an intense, bright blue. The third fraction was brown in visible light and bright gold in ultraviolet light; the fourth line was faint blue in ultraviolet light. The infrared spectra of the four fractions (Fig. 6) produced identical patterns, fractions 1 and 4 being weak due to low concentrations. If these were isomers they could not be simple structures like xyenols, etc., which differ in substitution around the benzene ring and thus give rise to markedly different infrared spectra.

The materials may well be short-chain structures which resemble the parent cured resin to some extent and differ from each other largely in molecular weight. This would explain the similarity of their infrared spectra and their separation by elution, due to differing solubilities in the eluants used. The golden color of the third fraction may be due to some loose intermediate being formed with acetic acid.

Liebig and Lassaigne sodium fusion tests on materials not subjected to thin layer chromatography gave uncertain results, but infrared spectra on the precipitates gave some suggestion that nitrogen compounds may be present in the pyrolysis products.

**Analysis of Solid Residues Condensed on the Pyrolyzer Tube.** These materials were split into two sets with two samples in each, the samples being collected from pyrolysis at oven temperatures of 140 and 185°C. For the first two samples the materials were first extracted with carbon disulfide prior to acetone extraction, the second two were extracted only with acetone (Table I).

The carbon disulfide extractions were evaporated to dryness and infrared spectra taken on smears. A portion of each acetone extract was dried

TABLE I

Sample	Material	Oven temperature, °C.	First extraction	Second extraction
A	Resin A	140	Carbon disulfide	Acetone
B	Resin A	185	Carbon disulfide	Acetone
C	Resin A	140	—	Acetone
D	Resin A	185	—	Acetone



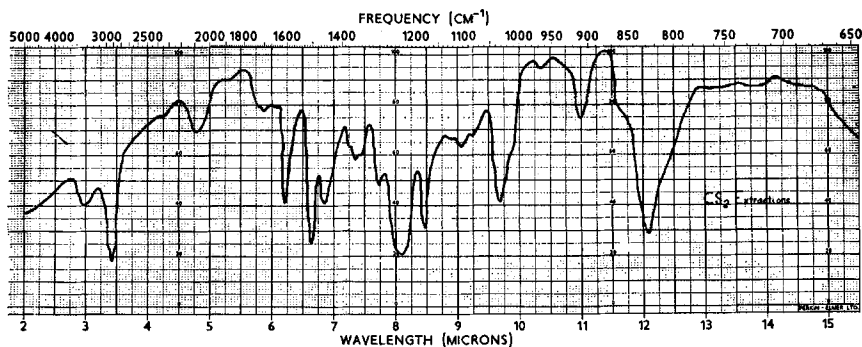


Fig. 7. Infrared spectrum of carbon disulfide extracts of pyrolysis residues from samples A and B.

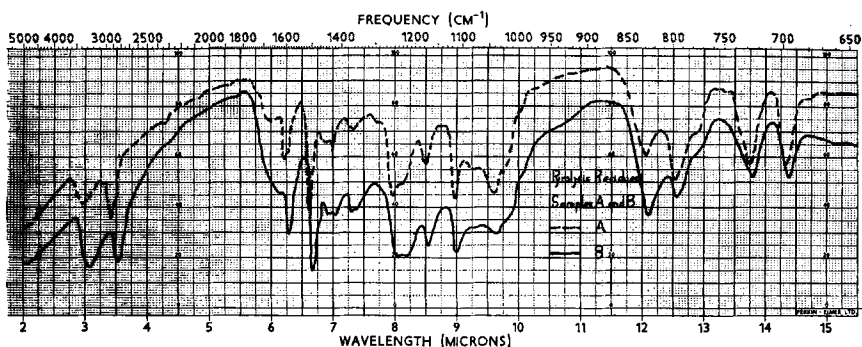


Fig. 8. Infrared spectra of acetone extracts of pyrolysis residues from samples A and B after carbon disulfide extraction: (---) sample A; (—) sample B.

(anhydrous copper sulfate), filtered, and evaporated, KCl disks being made using the residual material. Infrared spectra were then obtained for the unseparated acetone extracts. The remainder of the acetone extracts of each sample were separated by thin layer chromatography (absorbent phase silica gel H, eluants *n*-hexane and isopropyl alcohol in ratio 6:3). These separated fractions were treated as for the pyrolysis products, KBr disks made, and infrared spectra obtained.

The carbon disulfide extracts of samples A and B were identical (Fig. 7) and bore a striking resemblance to the cured resin structure, except that epoxide peaks appeared at 910 and 860  $\text{cm}^{-1}$ . This may be due to the residual epoxide structures from the cured compound which form endgroups to fragments otherwise similar to the parent compound. These materials appear to be preferentially soluble in carbon disulfide. The amount of carbon disulfide material is very small, and a number of solid residues had to be extracted to obtain enough material for an infrared spectrum.

Infrared spectra of materials from the acetone extraction of samples A, B, C, and D (Figs. 8 and 9) all gave a characteristic pattern from 1150 to 650

cm.<sup>-1</sup> with a few minor variations in intensity and position of some of the peaks.

Samples A, B, and C appeared to have secondary hydroxyl absorptions at, or near, 3350, 1360, and 1110 cm.<sup>-1</sup>, together with aromatic absorptions at, or near, 1600 and 1500 cm.<sup>-1</sup>. Ether phenol or aryl ether absorption was observed at 1250 and 1200 cm.<sup>-1</sup>, together with C—CH<sub>3</sub> near 1350 cm.<sup>-1</sup> and C(CH<sub>3</sub>)<sub>2</sub> near 1110 cm.<sup>-1</sup>.

Sample D had no secondary hydroxyl or aryl ether absorptions, but the pattern from 1150 to 650 cm.<sup>-1</sup> was still present, together with terminal double bond (—CH=CH<sub>2</sub>) absorptions at 3120, 3040, near 1800, 1600, 1420, 1330, and 990 cm.<sup>-1</sup>. One peak expected at 910 cm.<sup>-1</sup> was inexplicably missing.

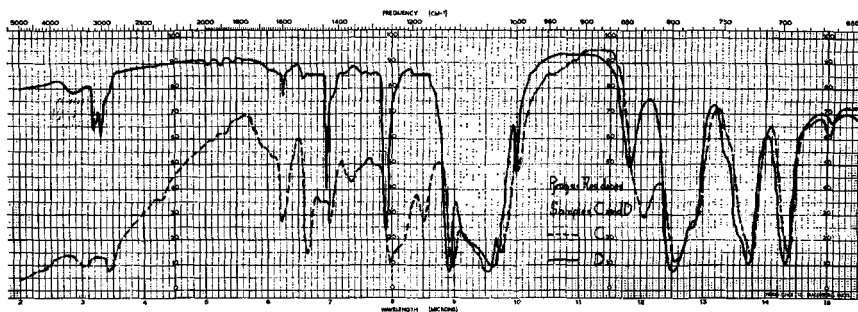


Fig. 9. Infrared spectra of acetone extracts of pyrolysis residues from samples C and D after carbon disulfide extraction: (---) sample C; (—) sample D.

The characteristic pattern of acetone extracts from 1150 to 650 cm.<sup>-1</sup> includes the region of main skeletal vibrations, and this implies that the various samples examined resemble each other in some way, but do not resemble the cured resin. Samples A and C (oven temperatures 140°C.) were very similar, in spite of carbon disulfide extraction in the case of sample A, whereas B and D had a distinct difference from each other. The reason for this is not clear.

Thin-layer chromatographic separation on all the samples, followed by infrared spectra in the usual way, separated the materials into component fractions having similar spectra to the parent sample. In samples A, B, and C, the carbonyl peak seemed to be much enhanced by the process of thin-layer chromatography, and this may well have been due to oxidation by atmospheric oxygen.

The infrared spectra of a number of model compounds were examined for reference purposes, but no correlations were found (1-chloro-2,4-dinitrobenzene pyridine, quinoline, methylcyclopentadiene, isopropyl phenol).

Infrared spectra of redistilled acetone used in extractions and also of the silica gel H and aluminum oxide HF234 used in thin-layer chromatography were examined as a precaution against contamination.

Solid pyrolysis residues which had been in existence for 3 weeks were examined with an acetone solution of 2,2-diphenyl-1-picryl hydrazyl. This material formed a dark purple solution in acetone and was stable for several days. On treatment with the solid pyrolysis residues the purple color was rapidly discharged, leaving the characteristic light brown solution obtained when extracting pyrolysis solid residues with acetone from the pyrolyzer tube.

This result indicates the presence of relatively stable free radicals in the solid residues condensed on the pyrolyzer tube. This confirms the ESR results of Neimann et al.<sup>11</sup>

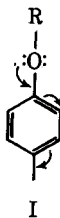
The following important points in the experimental findings should be stressed: (1) the tarry residues contain relatively stable free radicals; (2) the tarry residues contain materials of very similar structure to the parent resin, probably not highly degraded; (3) the tarry residues on the tube contain materials having secondary hydroxyl groups, and materials are also present having a terminal double bond; (4) certain materials obtained emerging from the column contained no secondary hydroxyl groups, but did show evidence for *trans* —C=C— structures.

There appears to be a spectrum of degraded products, from oligomers similar to the resin, nondehydrated products, dehydrated products, and finally smaller molecules, probably such as phenol.

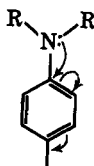
## DISCUSSION

For an epoxide resin to degrade there must be an initial rupture of bonds; what evidence we have suggests this is primarily homolytic, to produce free radicals which undergo further reactions. These may be expected to be of a complex nature.

Some ideas on primary fission may be obtained by considering in turn the bonds present in the epoxide resin under examination.



In the structure represented by an aryl ether (I), the electron shifts will be controlled by the balance of the negative inductive effect of the oxygen atom, with the positive mesomeric effect tending to move electrons into the benzene ring. The balance is such that a high electron density may be expected in the oxygen-phenyl bond, with an expected increase in bond strength.



II

A similar situation exists in the case of the aryl amine group (II), except that the negative inductive effect of the nitrogen atom is relatively weaker than the mesomeric effect. This gives a relatively smaller electron density than in the O-phenyl bond. Nevertheless, because of the above considerations, we may expect the O-phenyl bond and the N-phenyl bond to be stronger than the other bonds, the O-phenyl bond being the stronger of the two.

Bond strengths for other bonds not directly attached to benzene rings are quoted as follows: C-N, 66 kcal./mole; C-C, 80 kcal./mole; C-O, 87 kcal./mole; C-H, 98.2 kcal./mole.

In addition to this, structure such as  $\text{CH}_2\text{-C}_6\text{H}_5$  and  $\text{C}_6\text{H}_5\text{-C}(\text{CH}_3)_2\text{-C}_6\text{H}_5$  may be considered as complete entities.

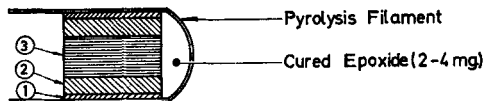
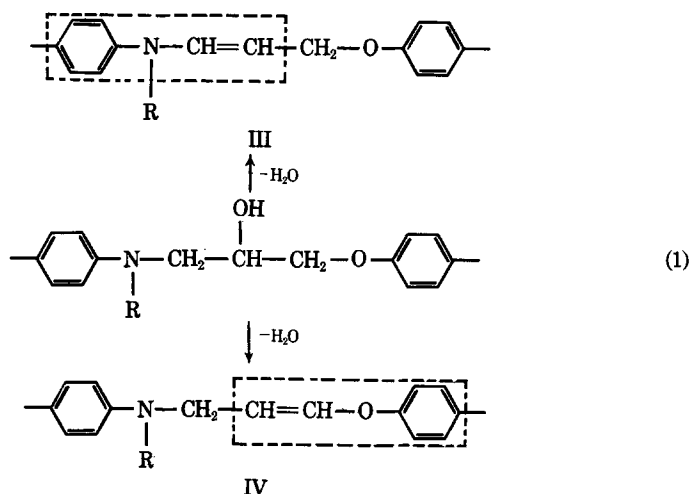


Fig. 10. Schematic representation of resin placed in pyrolysis filament.

The first of these structures may be slightly stronger than the C-C bond due to hyperconjugation of the methylene structure and the benzene ring. The second structure is subject to steric strain and we may expect the main chain C-C bonds to be weakened. These bonds and the aliphatic C-N bonds thus appear to be the initially weak points for fission.

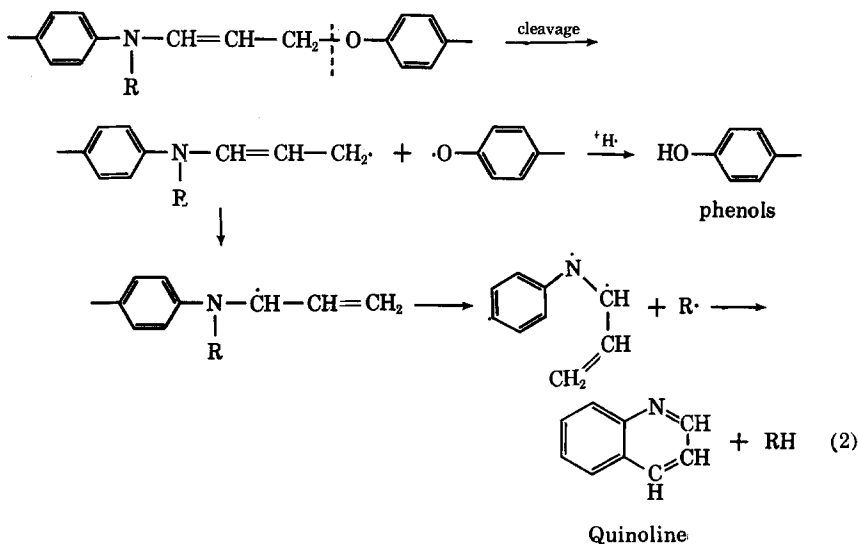
We may thus postulate that primary degradation occurs at the N-C bond and probably the  $\text{C}_6\text{H}_5\text{-C}(\text{CH}_3)_2\text{-C}_6\text{H}_5$  bonds. This may be expected to occur by homolytic fission. Complex secondary reactions will then occur, the nature of these will depend on temperature, this in turn depends on the proximity of an element of volume of the resin to the hot wire. One may, as a first approximation, represent the situation of the pyrolysis method by Figure 10. Volume 1 is material adjacent to the filament, which receives the longest heat treatment, at the highest temperature. This will undergo more secondary reactions and provide small molecules of lower boiling point, which may go into the GLC column. Volume 2 would provide material less broken down in structure, some of which would be volatile and go up the column, but some of which would condense on the pyrolyzer tube and become a solid residue. Volume 3 may contain material degraded to a lesser degree.

One of the initial reactions may be supposed to be dehydration. Lee<sup>2,7</sup> has evidence for water as a reaction product, and postulates this step [eq. (1)].

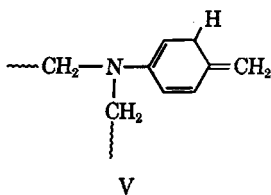


Within the dotted lines on the formulas delocalization may occur, giving an added stability to those groups of atoms. Structure IV may be preferred, due to the enhanced negativity of the oxygen atom and the improved possibilities of delocalization with the double bond. A *trans* double bond would be preferred for steric reasons. We have evidence that this structure does occur in the pyrolysis products; in the solid residue there is partially degraded material in which dehydration has not occurred. Here we may suppose a number of tertiary amine structures breaking down, giving secondary amines. Most of the structure would still resemble the cured resin, as was found in the carbon disulfide extracts. Rupture of C—N (aliphatic) bonds may well precede dehydration reactions, but only to a limited degree, and largely to give secondary amines, for which there is evidence. Incomplete cure will also account for the presence of secondary amines.

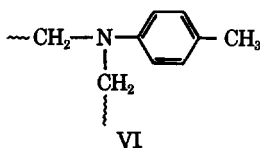
Degradation of structure III may be envisaged as shown in



The free radical produced by the cleavage of the diphenylmethane group could well be resonance-stabilized (V)



or alternatively extract hydrogen from the polymer to form such structures as VI.

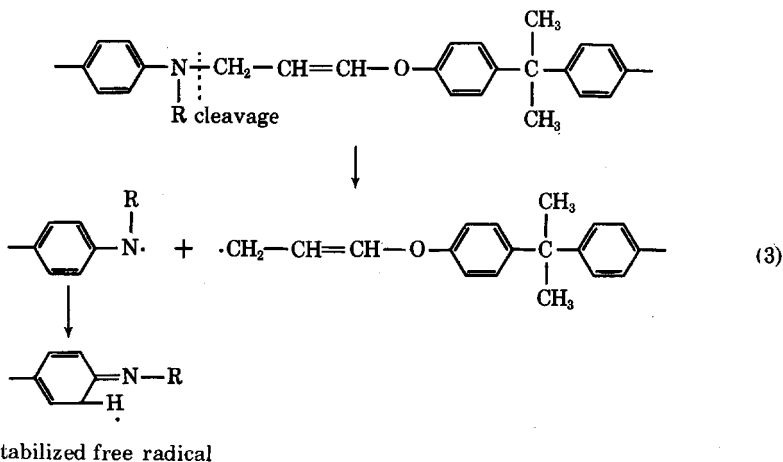


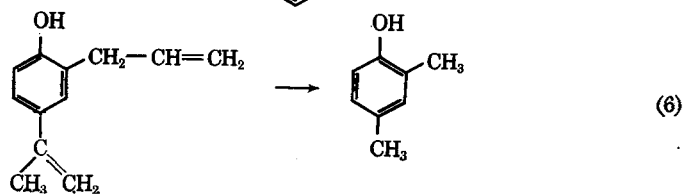
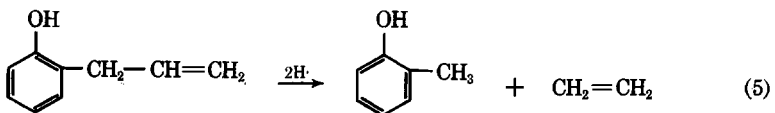
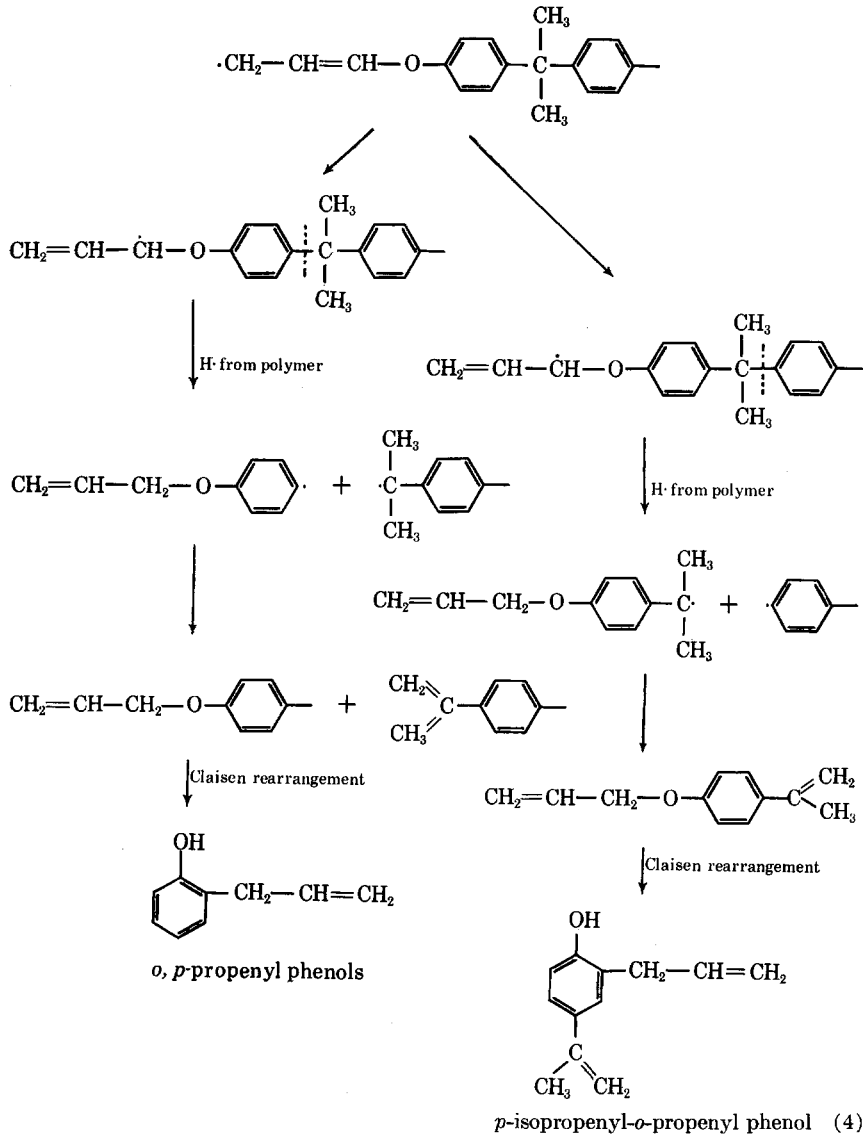
Certainly there is evidence, both from ESR and also from reaction with 2,2-diphenyl-1-picryl hydrazyl that resonance-stabilized free radicals do occur in the thermal degradation of epoxides.

Structure IV may degrade according to the scheme shown in eqs. (3) and (4).

These materials would most likely undergo more secondary reactions. Total removal of propenyl groups would produce phenol, for which there is evidence quoted in several other papers. Breakdown to give methyl groups might also be expected [eqs. (5) or (6)].

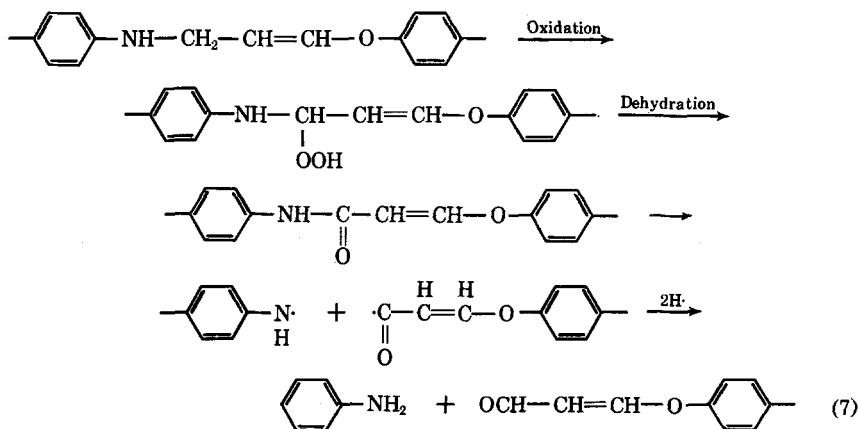
Such reactions would account for the presence of cresols and xylenols. More drastic breakdown in secondary reactions could even lead to the formation of simpler structures such as benzene and toluene. Gases such as methane or ethylene may be expected.





The initial dehydration step postulated by Lee<sup>2,7</sup> now seems to rest on definite evidence, and our proposed schemes incorporate this step, the notion of preferential breakdown at ether groups seems theoretically doubtful and we have suggested other reactions. In the nature of things these must be somewhat speculative; the presence of resonance-stabilized free radicals seems to rest on solid evidence, however, These exist in the solid residues, and very probably constitute the nitrogenous part to a large degree. There is evidence for the existence of material not degraded to a great extent, which contains a great deal of the original resin structure and where the dehydration reaction has not yet occurred. We thus have a spectrum of products varying from small molecules, of the phenol or cresol type, through to materials not greatly differing from the parent resin, except that some N—C linkages have been broken. The extent of degradation is related, in our opinion, to proximity to the hot wire.

Though the intention of the work was to examine nonoxidative degradation, there is always the possibility that the original resin contains dissolved oxygen which is not completely removed. This would lead to a certain amount of oxidative degradation. Both in the thin-film chromatographic separation of pyrolysis products and in the solid residues there was infrared evidence for oxidized structures and what is more, oxidation increased during the separation procedure. Nevertheless, the actual size of the absorption peaks for carbonyl and amide indicated that the concentrations of these structures were small. The evidence suggests that possibly something similar to the oxidative scheme of Lee<sup>2</sup> was occurring to secondary amine structures [eqs. (7)]



to give primary amine and unsaturated aldehyde structures. The fact that this process seemed to be continued during the actual chromatographic separation, judging by relative infrared bond strengths, cannot be explained at present.

Aldehydic products may well arise largely from oxidative degradation, if this scheme is correct.



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### Résumé

Ce manuscrit décrit une étude de la dégradation d'une résine époxy purifiée, basée, sur l'éther diglycidique de bisphénol-A durcit avec le diaminodiphénylméthane. La méthode utilisée était celle de la pyrolyse au filament chauffé, suivie de chromatographie gazeuse. Une attention particulière a été consacrée aux problèmes des résidus solides formés dans le tube de pyrolyse et on a prouvé que ces résidus contenaient vraisemblablement des oligomères. Des radicaux libres stabilisés par résonance étaient également formés et vraisemblablement une déshydratation a lieu au cours de dégradation, ce qui avait été préalablement supposé par Lee. Un essai basé sur ces principes de départ est fait en vue d'expliquer la dégradation des époxydes sur la base d'un travail antérieur aussi bien que au départ des résultats décrits dans le présent travail.

### Zusammenfassung

In der vorliegenden Mitteilung werden Abbauversuche an einem diaminodiphenylmethan-gehärteten Bisphenol-A-diglycidätherepoxyharz beschrieben. Es wurde die Methode der Hitzdrahtpyrolyse mit darauffolgender Gaschromatographie verwendet. Besonderes Augenmerk wurde auf das Problem der festen Rückstände am Pyrolysenrohr gerichtet und es wurde festgestellt, dass diese wahrscheinlich Oligomere enthalten. Resonanz-stabilisierte freie Radikale scheinen ebenfalls gebildet zu werden, und es bestehen Hinweise, welche die ursprünglich von Lee entwickelte Vorstellung einer Dehydratisierung während des Abbaus unterstützen. Es wird versucht, mit Hilfe früherer Ergebnisse sowie der in dieser Arbeit beschriebenen eine grundlegende Theorie des Epoxydabbaus zu entwickeln.

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