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Degradation of Epoxy Polymers: 2—Mechanism of Thermal Degradation of Bisphenol-A Diglycidyl Ether

Norman Grassie & Marilyn I. Guy

Department of Chemistry, University of Glasgow,
Glasgow G12 8QQ, Scotland, Great Britain

&

Norman H. Tennent

Glasgow Museums and Art Galleries, Kelvingrove,
Glasgow G3 8AG, Scotland, Great Britain

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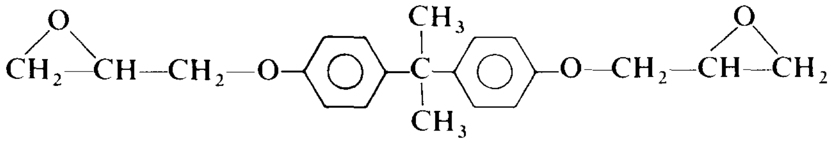
ABSTRACT

In a previous paper, some 15 compounds were positively identified among the products of thermal degradation of bisphenol-A diglycidyl ether. The structures of an additional 22 compounds, all aromatic, were speculated upon on the basis of mass spectral analysis. In the present paper, mechanisms are proposed to account for all these products and the characteristics of their formation in the overall degradation process.

INTRODUCTION

In the first paper of this series,[1] the principal characteristics of the thermal degradation of bisphenol-A diglycidyl ether,



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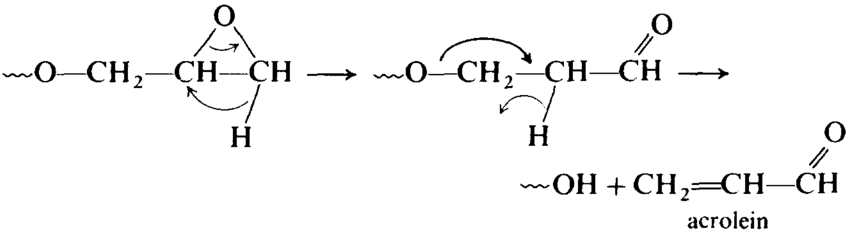
at temperatures up to 500 °C, were described. The products of degradation were separated and the more volatile were identified principally by gas chromatographic and mass spectrometric techniques. The most abundant were acrolein, acetone, allyl alcohol, water and phenol with small amounts of more volatile products, carbon monoxide, methane, carbon dioxide, propylene and a trace of ethylene, which were formed by further thermal degradation of the first three. The three cresols, xylenols (especially 3,4-xylenol), 4-isopropylphenol and probably ethylphenol were also identified in significant amounts.

A series of less volatile compounds was also formed and subjected to combined gas chromatography and mass spectrometry (GC/MS). None of these was positively and unequivocally identified but their mass spectral characteristics combined with a knowledge of the structure of the resin allowed extensive speculations to be made about their chemical identities. These suggested structures were all aromatic and are identified in this, as in the previous, paper by the numerals VI–XXVII.

In the present paper, mechanisms are proposed to account for all these products and the characteristics of their formation in the overall degradation process.

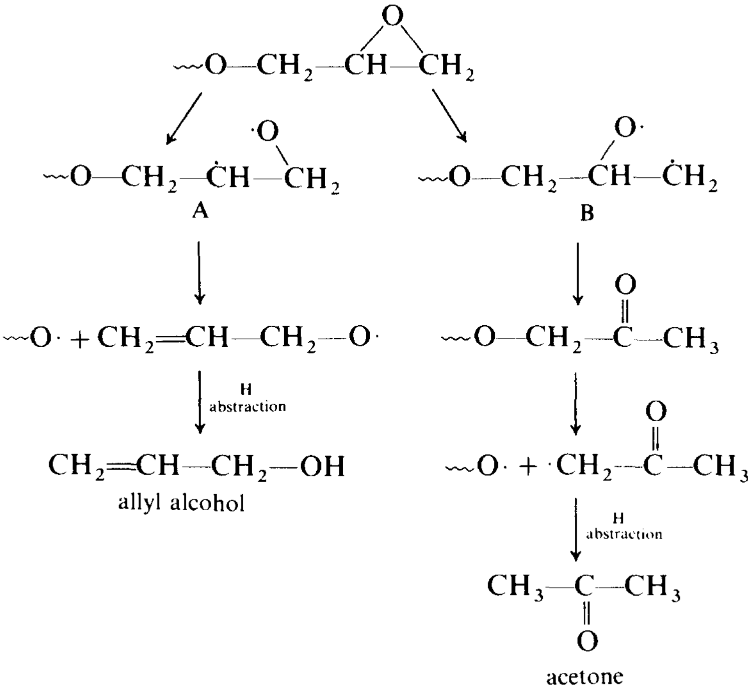
DISCUSSION

Acrolein is the most abundant volatile product in the earliest stages of degradation, at about 280 °C, and is most probably formed by isomerisation of epoxy groups to form a terminal aldehyde structure, followed by further rearrangement to liberate acrolein (reaction (1))



(1)

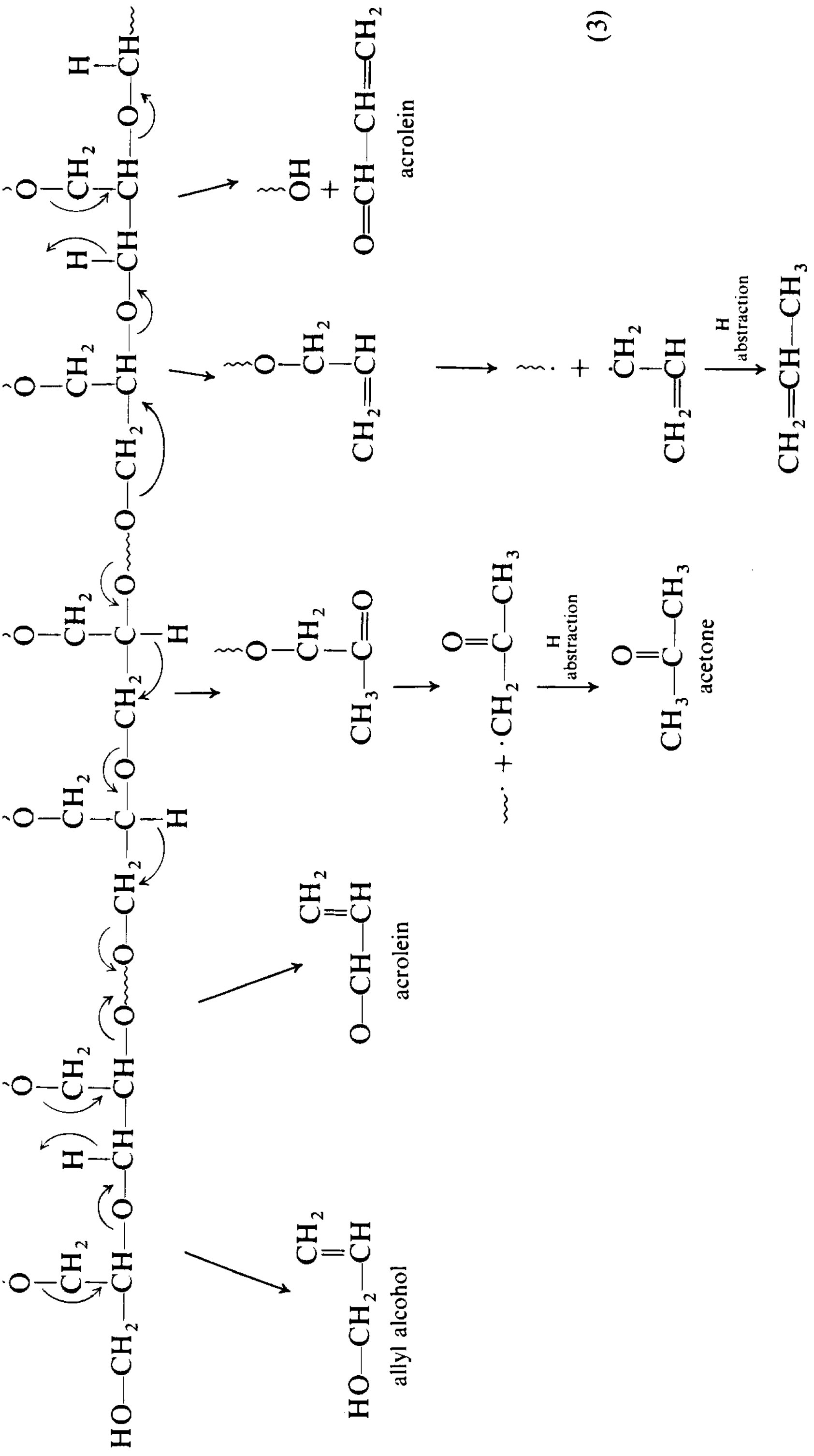
The other two principal volatile products, allyl alcohol and acetone, are also clearly associated with the epoxy groups and may be accounted for by reaction sequences (2) following C—O bond scission.



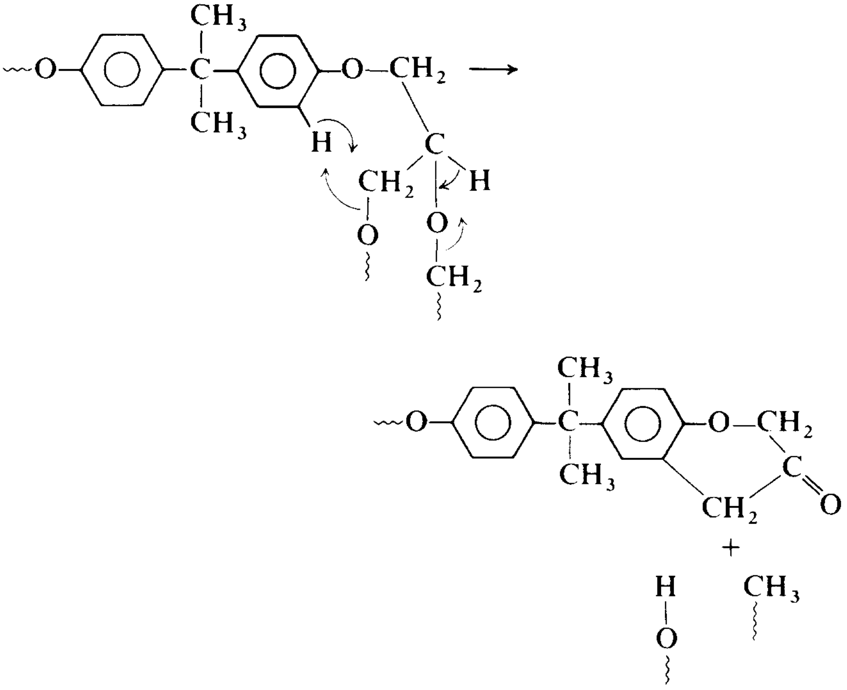
(2)

When the temperature is increased to 300–320 °C, linking up, or polymerisation, of the resin molecules occurs through the epoxy groups. This is almost certainly due to the interaction of diradicals A and B (see above) following C—O bond scission. If the oxygen and carbon ends are designated the heads and tails respectively of these two diradicals then the links between adjacent epoxy structures may be of a variety of types. Thus although A_{HT} and B_{HT}, that is the head-to-tail structures formed from diradicals A and B respectively, are identical, A_{HHTT}, B_{HHTT}, A_HB_H, A_HB_T, A_TB_H and A_TB_T are all different. Although it would be interesting to speculate upon the proportions of various products which might result from the decomposition of all these structures, it is sufficient in the present context to indicate how one of them, A_{HT}, is likely to decompose (sequence (3)). It is assumed that the polymerised epoxy resin is terminated by hydroxyl groups.

An alternative rearrangement, involving the aromatic portions of the polymerised epoxy resin, could result in cyclic keto structures (reaction (4)).

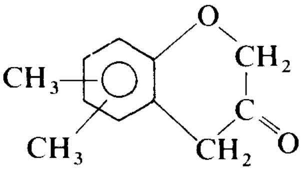

allyl alcohol
acrolein
acetone
H abstraction
acrolein
H abstraction
propylene

(3)

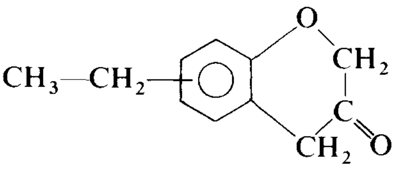


(4)

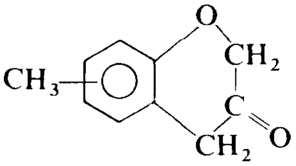
This structure would be the precursor of the three compounds XV–XVII formed on subsequent decomposition of the bisphenol-A residue.



XV

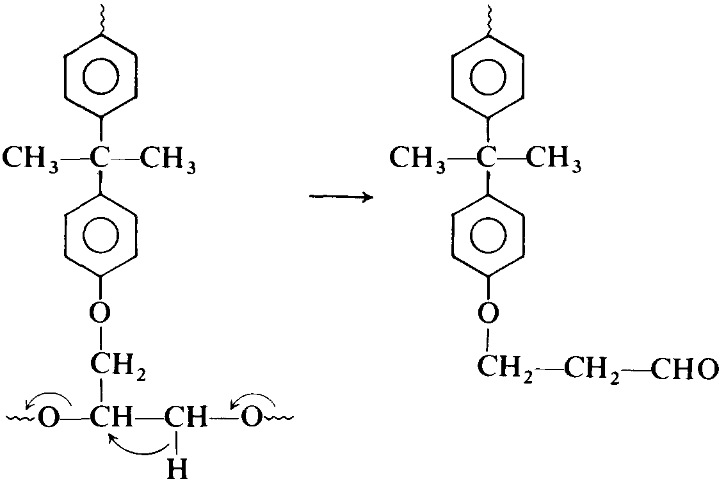


XVI

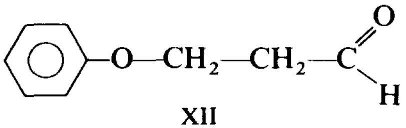


XVII

A slightly modified version (5) of the acrolein-producing rearrangement in reaction (3) will result in aryl aldehyde structures, from which XII could be later derived.

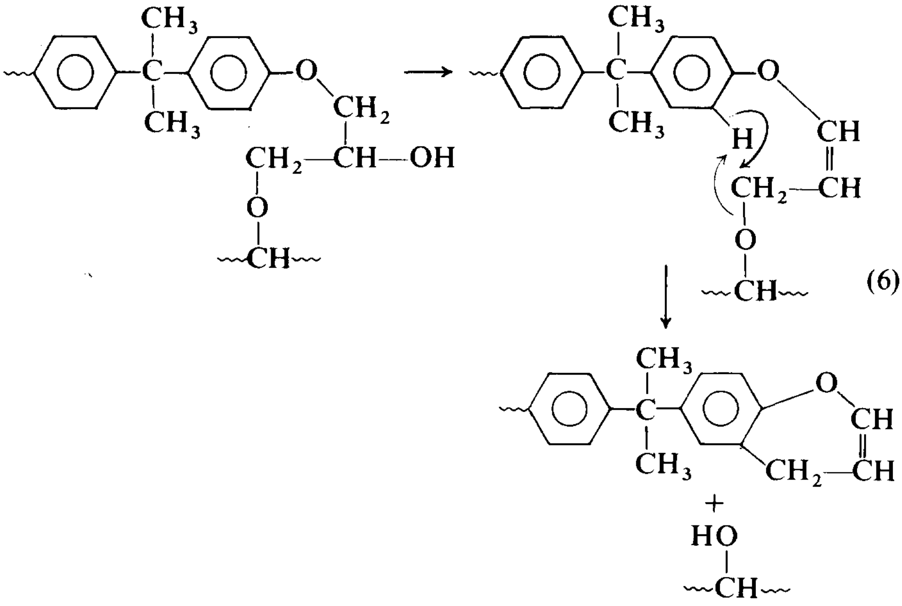


(5)



XII

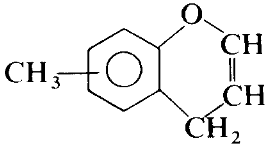
Water would be formed by dehydration of the terminal primary alcohol structures in the parent compound in reaction (3). Secondary alcohols,



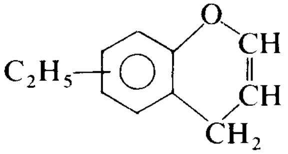
(6)

which would also be liable to dehydrate at elevated temperatures, could be formed by hydrogen abstraction after scission of an ether bond. The unsaturated structure thus formed could undergo cyclisation with the adjacent aromatic ring to form pyranyl rings (sequence (6)).

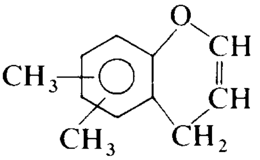
This would account for products VI, VIII, IX, XIV, XXV and XXVII on subsequent disintegration of the aromatic structure.



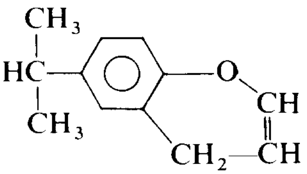
VI



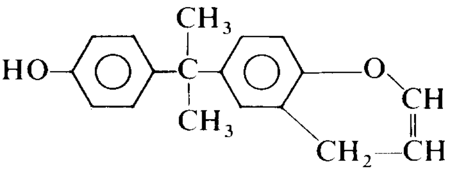
VIII



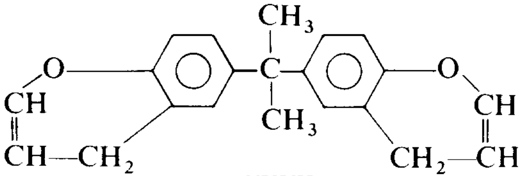
IX



XIV

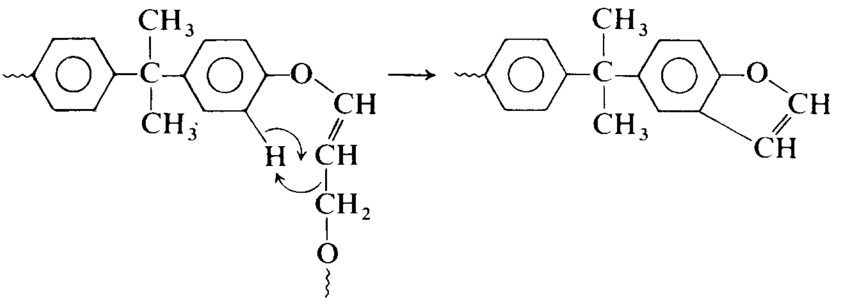


XXV

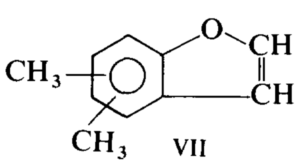


XXVII

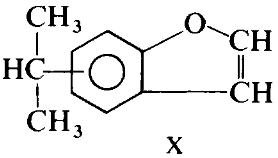
The unsaturated structure formed in the first step of reaction (6) must also cyclise (reaction (7)) to form furanyl structures, the precursors of products VII, X, XXIV and XXVI.



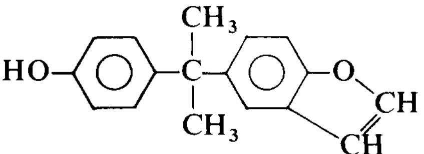
(7)



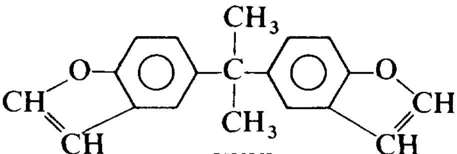
VII



X

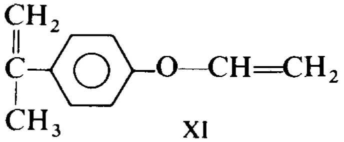


XXIV

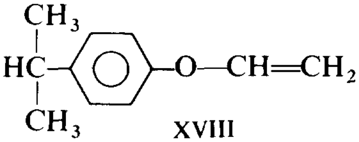


XXVI

On the basis of mass spectral data, *p*-isopropenyl-phenyl vinyl ether (XI) was proposed as one of the minor products of degradation of the resin and *p*-cumenyl-vinyl ether (XVIII) as possible, but less likely.

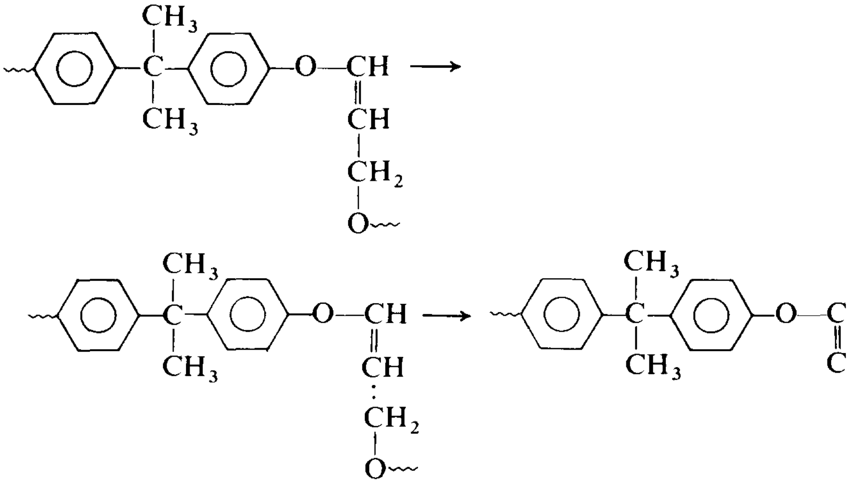


XI



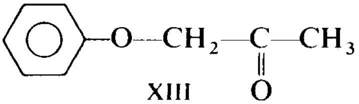
XVIII

It seems most likely that the formation of these compounds would depend upon chain scission adjacent to the double bond formed in the first step of reaction (6) followed by hydrogen abstraction sequence (8)) and, ultimately, decomposition of the bisphenol-A segment.



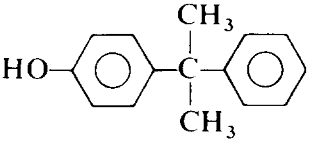
(8)

Compound XIII is another which seems possible on the basis of mass spectral data but was disfavoured in the previous paper.[1] This product

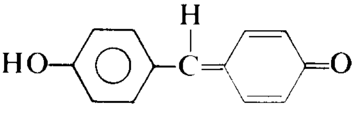


XIII

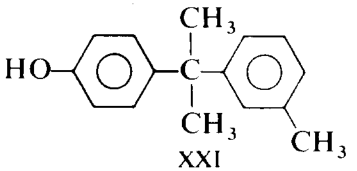
could be the result of decomposition at the bisphenol-A segment of the precursor of the formation of acetone represented in eqn (2). The yield would be expected to be quite low, however, since bond scission and hydrogen abstraction to form acetone should be expected to occur at a lower temperature than decomposition of the bisphenol-A segment.



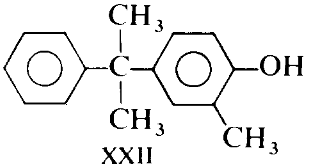
XIX



XX

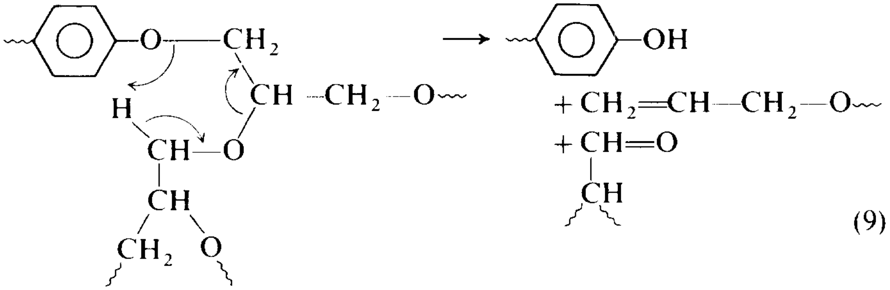


XXI



XXII

Many of the decomposition products of the resin are phenolic; for example, phenol, *o*-, *m*- and *p*-cresols, 3,4-xylenol, 4-isopropylphenyl, XIX, XX, XXI and XXII and bisphenol-A. A number of reactions involving four-, five- and six-membered ring interactions may be formulated to account for the formation of the phenolic hydroxyl group and reaction (9) seems to be among the more likely. The additional products of this reaction may clearly also be precursors of some of the other degradation products.



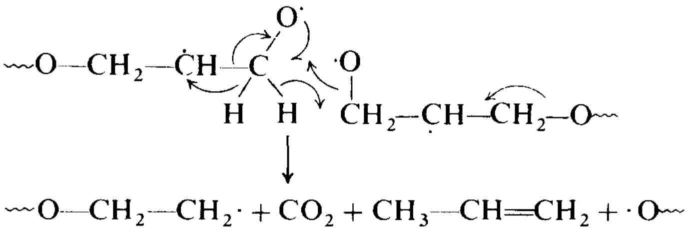
(9)

The principal products of degradation of bisphenol-A were shown in the previous paper to be methane, phenol, 4-isopropylphenol and 4-isopropenylphenol together with small amounts of propylene. Since methane is formed in relatively high yield from both bisphenol-A and the resin, it is clear that scission of the *C*-methyl bonds is favoured compared with *C*-aryl bonds in the decomposition of the bisphenol-A residues. The occurrence of a certain proportion of the latter must be assumed, however, in order to account for the 4-isopropyl- and 4-isopropenylphenols. Since only small amounts of propylene are formed in the decomposition of bisphenol-A, this is clearly only a minor source of the compound during decomposition of the resin. The relatively large concentration of methyl radicals in the degrading system will also account for the large number of products which are methyl-substituted in the aromatic ring.

It is clear from the data in Table 1 of the previous paper that certain of the non-condensable products of degradation of the resin may be derived from the further degradation of certain primary products as they diffuse through the hot degrading resin. Thus it was shown that carbon monoxide, ethylene, methane, propylene, carbon dioxide and a trace of formaldehyde are all formed during the thermal decomposition of acrolein and allyl alcohol.

The most obvious source of carbon dioxide from both the resin and its decomposition products, acrolein and allyl alcohol, is oxidation due to the presence of a small amount of oxygen in the system. This seems unlikely, however, especially in the resin, the degradation of which was carried out under carefully controlled vacuum conditions.

Alternatively it may be suggested that interaction occurs between pairs of epoxy groups (reaction (10)), although this kind of reaction, if it occurs, would almost certainly do so in a number of steps.



(10)

REFERENCE

1. N. Grassie, M. I. Guy and N. H. Tennent, *Polym. Degrad. and Stab.*, **12**, 65 (1985).