

Proposed Mechanism for the Thermal Decomposition of Phenolic Polymers

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Structure of Highly Crosslinked Carbonized Thermosets

Graphite is one of the most well known forms (or allotropes) of carbon owing to its anisotropic, hexagonal close packed structure with the characteristic '*d*' spacings responsible for so many of its unique properties. These '*d*' links, connecting planes of hexagonally bonded carbon atoms by way of van der Waals forces, permit slipping between the planes (hence, graphite's lubricating properties) and ultimately affect the allotrope's anisotropic properties somewhat differently than other forms of carbon. Carbon atoms in these planes are covalently bonded to three other carbons via trigonal planar sp^2 hybrid orbitals and donate a fourth electron to the delocalization pool responsible for graphite's high conductivity along these planes.

On the other hand, pseudo-amorphous carbon structures being joined via tetrahedral sp^3 orbitals include carbon black, petroleum coke and the green carbonized forms of oil and coal tar pitch. These more common forms are considered to be 'soft' carbons, since heating to $> 4000^\circ\text{F}$ will transform their microstructures into graphite-like arrangements. During the heating cycle, these soft carbons will go through a temporary liquid crystal mesophase state somewhere in the range $750\text{-}950^\circ\text{F}$ with a limited mobility that facilitates the formation of graphitic layer planes leading to a pre-graphite lattice. Continued heating into the graphitization temperature regime ($\sim 4000^\circ\text{-}4500^\circ$) diminishes the amorphous sp^3 bonding nature as the structure becomes rich in aromatic sp^2 orbitals. Unless oxidation pre-treatments are applied, all amorphous carbon structures that ultimately become graphitic must pass through a liquid mesophase state before developing substantial hexagonal sp^2 character.

Now the char remnants of densely crosslinked thermoset polymers comprise a unique category of amorphous carbon, referred to as 'hard' carbons, which permit no movement or rearrangement of the atoms during heating. Consequently, hard carbons will not undergo reconstructive transformation under ordinary graphitization conditions. The macromolecules comprising the organic precursor for these types of non-graphitizing structures are fixed in space due to the extensive crosslinked network established during the polymer curing process. Not surprisingly, the higher the density of crosslinks in the cured network, the harder carbon the polymer becomes when pyrolyzed. In general, all crosslinked thermoset polymers form very hard carbons upon carbonization. It is important to make of the proper terminology which refers to these forms of hard carbons as 'glassy' or 'vitreous' carbon since they appear to contain very high degrees of amorphism and exhibit fractured faces characteristic of glass materials. Such glassy hard carbon precursors include the phenolics, epoxies, polyesters, nylons, acrylonitriles, rayons, and so on.

Glassy carbons often have the appearance of a 'black glass' and are more reminiscent of ceramics than graphite. In contrast to graphite and most other carbon forms, some of the most striking property differences associated with glassy carbons include much lower thermal and electrical conductivities (while the existence of aromatic electrons still prevails in the local structure, there are no directional planes throughout the macrostructure to facilitate conductance), increased resistance to thermal and mechanical shock (the amorphous/glassy structure absorbs and deflects shock waves instead of transferring them), and chemical inertness (while all other carbon forms are susceptible to thermal oxidation and the action of super acids, glassy carbons exhibit the greatest resistance to chemical degradation).

Many thermoplastics and most linear aliphatic polymers as well as simple and fused aromatics (mesophase pitches) will readily undergo graphitization while most thermosets (like phenolic resin) will not graphitize even at temperatures of 5500°F and above. In addition, contrary to industry perceptions, common thermoplastic fibers comprised of PAN and rayon polymers do not undergo graphitization. This is due to the pre-carb oxidative stabilization step applied to these fibers which exposes them to low levels of oxygen at low temperature. Such exposures result in the formation of crosslinks in the green polymer, converting it into a thermoset, and are necessary in order to obtain an infusible polymer prior to the carbonization step. While there may be a few regions within these fiber structures that almost attain graphite-like order, stabilized PAN and rayon fibers are classified as hard carbons which are high in glassy-like structures and do not pass into mesophase or graphitize.

In contrast, soft carbons derived from pitch resins and fibers contain no crosslinks, will easily pass through mesophase and graphitize. The difference between graphitizable and non-graphitizable carbon can be visually appreciated by examining Figure 1 below, courtesy of some of the research done by Peter Harris^[3], which shows images of (a) sucrose and (b) anthracene carbonized at 4200°F. Note that sucrose is similar to rayon, which is made up of beta-linked glucose units (cellulose) and anthracene is analogous to coal tar pitch . . . except in these pictures, the rayon was subjected to oxidative stabilization prior to carbonization while the anthracene was not.

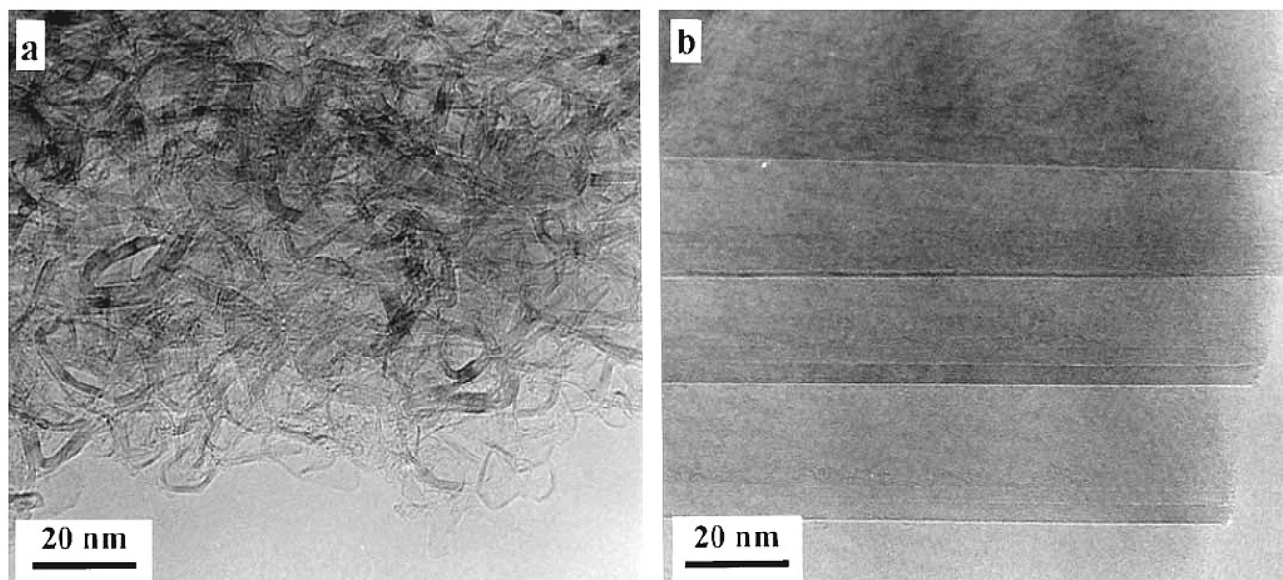


Figure 1. Micrographs of (a) sucrose carbon and (b) anthracene carbon following heat treatment at 4200°F.

Microstructures of carbonized thermoset resins seem to retain a substantial degree of resemblance to the amorphous isotropic character formed during cure/crosslinking processing in the organic phase. Also, these glassy chars are less porous than bulk graphite and the structure of their porosity network appears to be highly influenced by the specific conditions implemented during the cure process (such as applied pressure and heating rate during autoclave cure). Independent observations have indicated that the basic nature of the porosity network and pore interconnectivity are established during the polymer curing stage (or article fabrication process) . . . and the subsequent escape of pyrolysis gases appears to occur predominantly as the existing pores are widened and enlarged, which leads to even higher porosity and interconnectivity. Ablative diffusion or etching as pyrolysis gases are forced to exit the system also create additional pores and interconnections as they become an extension to the existing pore network.

In glassy carbon bodies, there is evidence that a small level of closed porosity is created during the pyrolysis process which has been characterized via small angle-ray diffraction as hemetically sealed voids or bubbles dispersed within the glass. These closed regions are much less significant in a charred matrix spread out within a porous composite network or a polymer which has been formed into a thin filament and then carbonized. In any case, it should be realized that the carbonization process transforms an organic carbon-based material into an inorganic carbon form, so the methods for describing these two phases must transcend from organic to inorganic chemistry . . . almost.

Oxidation and Pyrolysis are Parallel Processes

It should be realized that the structure of phenolic substrates contains reaction water, absorbed moisture, hydroxyl groups, perhaps air pockets and other sources of oxygen. Thus, to varying degrees, oxidation/combustion and inert pyrolysis must be coexistent processes during the thermal decomposition process, especially in the early degradation stages. Even during a pyrolytic operation conducted entirely under inert conditions, initial decomposition reactions will inevitably include oxidation of the phenolic matrix. Universally, the combustion products of organic matter are typically water and carbon dioxide. Also, as inert pyrolytic decomposition progresses, oxygen radicals are generated which will induce oxidation reactions with polymer sites on their way out. In an oxidizing environment on the other hand, combustion is obviously a major player in the decomposition process, but pyrolysis is also taking place in regions of the network where oxygen is not present or has been ‘starved’ out of the network, and this can be substantial.

No doubt, the higher the degree of pyrolysis, the greater the char yield will be. In a number of previous studies conducted by the author examining Borden resols^[2], neat phenolic resin samples cured under pressure have repeatedly yielded around 56% char remnant after almost complete conversion (95-98%) and a measured true density of 1.43g/cm³. Literature TGA results have frequently noted ~ 50% char yields for cured phenolic resins^[4]. Without the application of pressure during the curing cycle, the release of solvents and condensation volatiles can become somewhat violent after about 200°F resulting in significant resin loss. Decomposition products for oxidation and pyrolysis have some significant differences in the types of gaseous molecules emitted during the process. It goes without saying, decomposition gases are the sole reason for weight losses that occur during TGA tests and carbonization applications, regardless of the amount of solid char produced. While composition differences in char yield may be small for the two degradation processes, inert pyrolysis will favor the generation of carbon monoxide along with various hydrocarbons reflective of the original phenolic structure while oxidation and combustion will be characterized primarily by the release of CO₂ and water.

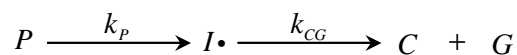
Thus, a proper treatment of the thermal degradation of phenolic networks must take into account the reactions and effects of both pyrolytic and oxidative degradation concurrently as well as independently, regardless of the decomposition environment and specific firing conditions. The majority of TGA-MS evidence indicates that oxidation is predominant during the first portion of the decomposition process and then pyrolysis products (cracking) tend to dominate the higher temperature portion of the cycle. Oxidation and pyrolysis reactions may appear to be consecutive phases from one perspective but they definitely have significant overlaps across the decomposition process. This point will be explored further later on.

It has been demonstrated that the thermal decomposition kinetics of cured phenolic networks are greatly influenced by the heating rate used during the carbonization process, particularly between about 300°C/min (570°F/min) and 500°C/min (930°F/min)^[5]. A number of TGA techniques are available to explore a variety of interesting test conditions during the heating cycle that can reveal much information about the mechanisms at work during the thermal decomposition process. Phenolic matrix composites used in ablative and nozzle liner applications see abnormally high heating rates (several thousand degrees in a couple of minutes) and it is not unusual for classical kinetics and thermochemistry expectations to fall short of a reasonable description of the actual phenomena taking place. Rapid carbonization and thermal shock effects are the primary topics for future studies in this series. This first paper is intended to explore the more classical approaches in describing the behavior of phenolic networks during carbonization and may serve as a starting point or baseline, if you will, for developing more appropriate models to better define the extremely rapid conversion of these materials during the rocket firing process.

One thing is fairly certain however . . . regardless of whether the firing sequence is fast or slow, ***the thermal degradation of phenolic polymers is a temperature driven, free radical propagating process.*** During the initial decomposition phase for a slow, steady state firing cycle, stable radicals will naturally form, rearrange and seek low energy states in accordance with classical thermodynamics. However, as the system temperature relentlessly increases throughout the heating cycle, less stable radicals become the inevitable intermediates and decomposition pre-products begin to deviate substantiately from traditional organic reaction analogs. Indeed, the lifetimes of transition state free radicals during solid state thermal conversion of plastic thermosets must be abnormally high.

Free radical chemistry is an extensive subject (and quite popular in recent years) dealing heavily with the concept of a single or lone electron in a given atom or molecule, and often treats di- and tri- radical species in special situations. In contrast, decomposition of a cured phenolic article (one big solid molecule) might contain thousands of reaction sites where free radicals are being generated as the network begins to break down into smaller contiguous fragments. Any given fragment would contain a multitude of cleavage points in which radicalized molecular groups are undergoing simultaneous decomposition reactions. In addition, it is suggested here that, during later stages of the decomposition process, single carbon atoms may themselves assume short lived tri- and quad-radical transition configurations. These concepts give new meaning to the term ‘di-radical’.

From a simplified perspective, thermal decomposition of a phenolic network might be represented as a two step, first order, unimolecular, irreversible reaction. As decomposition commences, the cured polymer P , degrades to form free radical intermediates $I\cdot$, which then react to produce carbonized resin char C and pyrolysis/combustion gases G . To be thorough, at least two cases would need be considered: (a) the radicalized intermediates are converted into char along a reaction path that also generates gases, and (b) the intermediate is converted into gases and char along independent pathways in parallel reactions. Another scheme might combine both cases as coexistent and/or parallel processes. This is probably more reflective of reality but is beyond the scope of this first report. For the present, consider the situation given in (a) . . .



In this scenario, the quantity of phenolic substrate decreases as free radical intermediates are generated and the concentration of radical intermediates decreases with the simultaneous formation of gases and solid resin char. Kinetically, the rate equations can be given as . . .

$$\frac{dP}{dt} = -k_p P \quad \frac{dI\bullet}{dt} = k_p P - k_{CG} I\bullet \quad \frac{dC}{dt} = \frac{dG}{dt} = k_{CG} I\bullet = k_{CG} CG$$

In some problems, the steady state approximation may be applied which would presume that the change in intermediate free radical concentration remains constant so that $dI\bullet/dt \approx 0$. This condition gives simply, $k_p P = k_{CG} I\bullet$ and $dC/dt = dG/dt = k_p P$. Now if W_0 is the initial weight of a TGA sample and W is the instantaneous weight as the sample undergoes conversion, then $W_0 = P_0$, $W = P + C$ and $W_0 - W = G$. Here, the degree of conversion shall be defined as $\alpha = 1 - W/W_0$ or $\alpha = 1 - W$ if the weight is normalized. Then the rate equation can be given as . . .

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

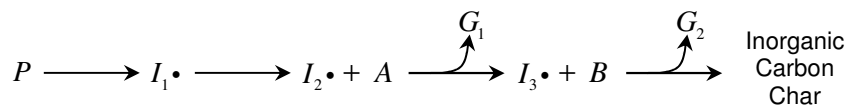
which becomes

$$-\frac{dW}{dt} = kW^n \quad (2)$$

where n represents the order of the reaction.

The assumption of steady state conditions is prevalent throughout the literature for many situations involving burning/combustion processes, pyrolysis and TGA of polymers. However this simplification may be invalid for applications dealing with abnormally high heating rates and rapid firing situations. These conditions will be dealt with in future studies.

Before proceeding, it should be noted that the reaction scheme given above is probably over simplistic. It is more likely that the actual mechanism involves the concurrent production of multiple gases, several intermediate radicals and a few compounds along any given pathway leading from the organic polymer state to the final char. Perhaps something like . . .



Now when the heating rate is known or specified, $\beta = dT/dt$, and the well known Arrhenius temperature dependency is incorporated into Eq (2), the result becomes . . .

$$\frac{-dW}{dT} = \frac{A}{\beta} \exp\left(\frac{-E_a}{RT}\right) \cdot W^n \quad (3)$$

where, as usual, A is the pre-exponential factor, E_a is the activation energy for the reaction (or group of reactions), R is the gas constant ($8.3144 \text{ J}^\circ\text{K}^{-1}\text{mol}^{-1}$) and T is the absolute temperature. This relation can be applied to dynamic TGA curves as will be attempted below. One must realize however, Eq (3) reflects the weight losses occurring due to generated pyrolysis gases and says nothing (that is, directly) about the char solids that are produced.

The kinetics of free radical polymer decomposition is a tricky subject due to the large number of possible conditions and parameters, each of which can have significant effects on the apparent reaction rates and activation energies. Even the particular kinetic model or analytical approach used can give vastly different results than another model. Thermal decomposition of phenolic networks via TGA has been the

subject of many studies over the years with the majority of those cases examining conditions of relatively slow, steady state conversion of small resin samples. In previous studies examining one of the Borden resol resins (the predecessor to Durite SC1008HC) a number of chemical/physical characterization methods were utilized including a series of dynamic TGA measurements conducted in nitrogen atmosphere^[2]. Some of those results have been reproduced here and are presented in Figures 3 and 4 which clearly illustrate the primary weight changes taking place when neat phenolic resin samples are heated from room temperature up to about 1500°F at 20°/min (~0.3°/sec). In these tests, the resin sequentially underwent (1) complete solvent evaporation, (2) full condensation cure and (3) pyrolytic decomposition in about a 40 minute time span.

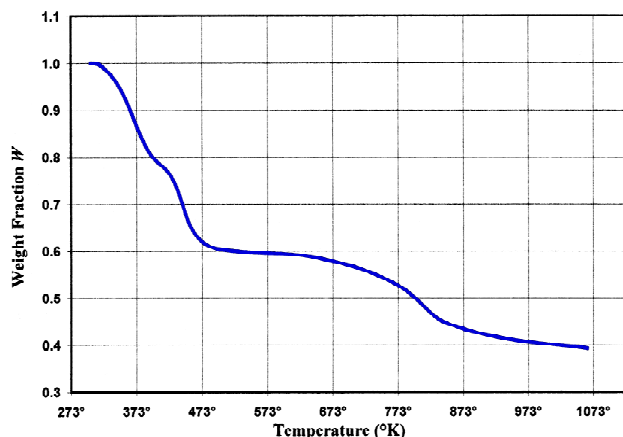


Figure 3. Dynamic TGA trace showing weight change vs. temperature for Borden phenolic resol.

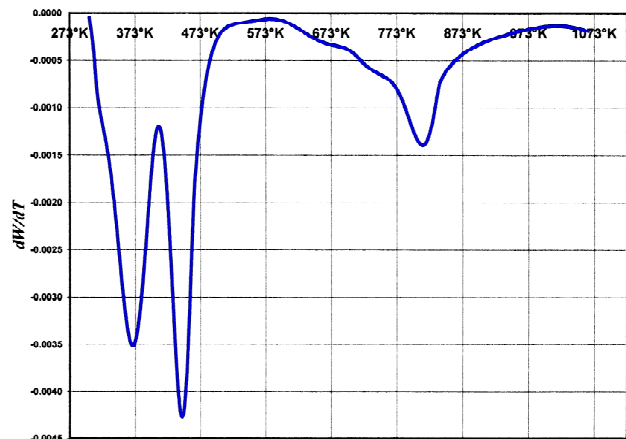


Figure 4. Derivative curve (dTGA) for TGA trace given in Figure 1 highlighting regions of maximum weight loss.

The first derivative curve shown in Figure 4 (denoted dTGA or dW/dT) illustrates the regions of primary weight loss across the applied temperature range where the peaks represent the inflection points along the original TGA curve. Moving from left to right (Figure 4); the first peak depicts the release of resin solvent (IPA) commonly used in HS resols at about a 30% level (boiling point 355°K); the second peak illustrates the condensation (polymerization/crosslinking) reactions that result as the resin undergoes thermal curing; and the last, broader peak, starting at about 580°K, represents the thermal decomposition range which includes pyrolytic conversion of the cured resin into glassy carbonized char and pyrolysis volatiles. More precisely, peak one is a measure of the weight loss that occurs as IPA boils out of the system, peak two measures the weight loss resulting from the release of condensation side product (water), and the third region depicts weight losses occurring as gaseous pyrolysis side products leave the system. Since the thermal decomposition (pyrolysis) process is the region of interest, it is worth while to study this region in greater detail. Figure 5 is a blow up of this range which highlights some special points of interest.

Examination of Figure 5 below permits the following observations. Prior to the primary region where the majority of decomposition occurs (midpoint 812°), there appears to be two minor sub-regions where perhaps early decomposition reactions are taking place, suggesting that the degradation process consists of at least three phases. Moving from left to right, let us denote these sub-regions as A, B and C respectively. The peaks or midpoint temperatures are indicated for each sub-region and reflect the point of maximum weight loss occurring in those sub-regions across the TGA test range. Notably, sub-regions A and B are not so apparent in the original TGA trace but are visibly detectable in the dTGA curve. As will be expanded on later, sub-region A (and maybe some of B) is believed to represent secondary combustion/oxidation reactions that precede or lead into the primary pyrolytic decomposition phase C.

However, one should bear in mind the that there is a considerable degree of overlap between the combustion and pyrolysis phases.

Many authors throughout the literature have made their data fit various modifications of Eq (3) by allowing the reaction order to assume values other than one (including fractions and negative numbers). However it is contended here, for this first simplified approach, that all the reactions (or phases) occurring follow first order kinetics and the order of unity will be assume throughout this treatment. The universal validity of Eq (3) across a broad spectrum of temperatures and reaction types could be debated with good reason however, its application to particular elements in this study have appeared to provide some useful information. Each sequence of reaction steps in a given phase will have a unique value for E_a and A where the sum of the three phases should give the overall E_a for the decomposition process.

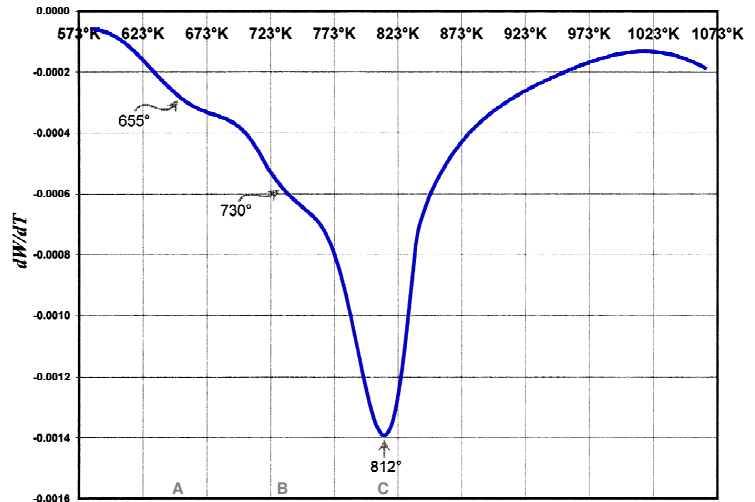


Figure 5. Decomposition region of dTGA curve given in Figure 2 showing particular points of interest.

Consider now our basic rate equation, Eq (3) with $\beta = 0.3^\circ\text{K/sec}$ and $n = 1$. As is commonly done, the equation is written in linear ‘slope-intercept’ form by taking logs . . .

$$\ln\left(\frac{-dW/dT}{W}\right) = -\frac{E_a}{R} \frac{1}{T} + \ln\left(\frac{A}{0.3}\right) \quad (4)$$

If applied intricately, this linear form of the weight-temperature rate law can be plotted and used to infer approximations for E_a (a component of the slope) and A (a component of the y-intercept) along segments where approximate ‘Arrhenius linearity’ prevails. Close examination of Figure 3 seems to indicate

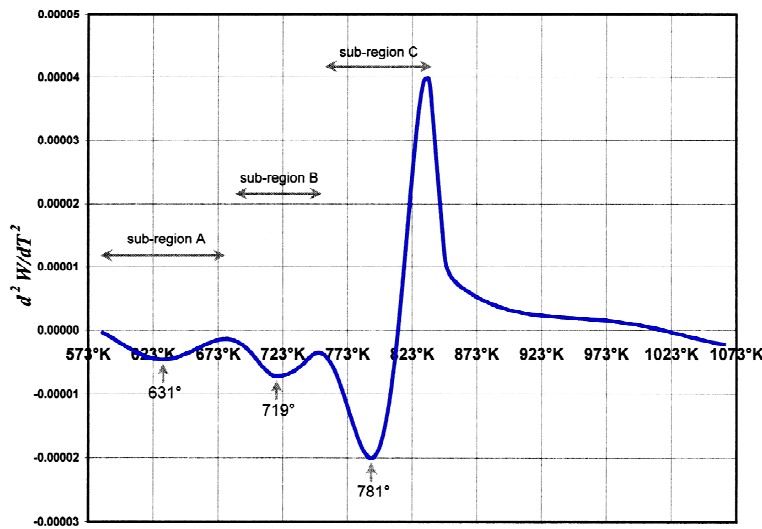


Figure 6. Second temperature derivative curve for the initial TGA trace indicating dTGA inflection points in the maximum acceleration segments of each sub-region.

that the most linear segments in dTGA occur prior to the TGA inflection points, midway between the start of each region and the maximum temperature points indicated. These particular segments represent the areas of maximum ‘acceleration’, if you will, for each region since they are the steepest down ramps occurring prior to the point of maximum weight loss. These acceleration points can be guessed from the dTGA curve or better yet, determined more precisely from the second derivative curve (denoted d²TGA or d^2W/dt^2) given in Figure 6 which illustrates the inflection points of the dTGA curve for sub-regions A, B and C.

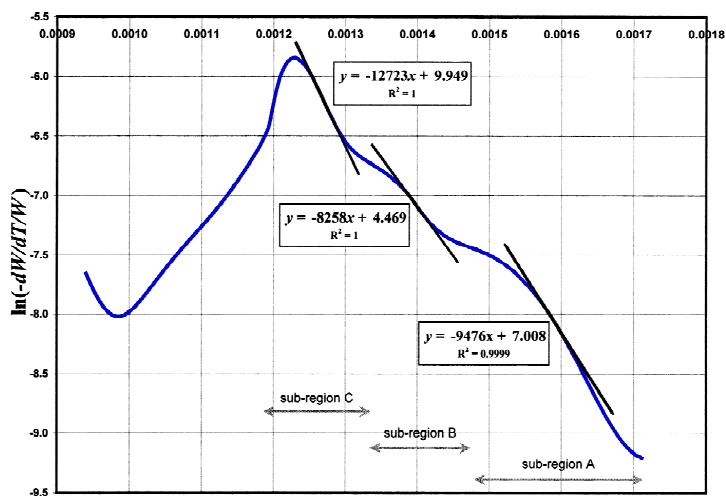


Figure 7. Composite plot of Eq (3) vs. $1/T$ across the entire decomposition range showing analysis of tangent lines at maximum acceleration points for each sub-region.

In a composite plot containing all three sub-regions, linear tangent lines at each of the dTGA maximum acceleration points (as highlighted in the d²TGA curve of Figure 6) can then be simultaneously evaluated to the linear form of Eq (4). A graph of . . .

$$\ln\left(\frac{-dW/dT}{W}\right) \text{ vs. } \frac{1}{T}$$

across the entire decomposition range is given in Figure 7 along with the tangent line analysis used for each sub-region as determined via linear regression techniques. With this method, the slope of the tangent line for each sub-region is equal to E_a / R and the y-intercept is simply $\ln(A/0.3)$.

Results from the analysis are given in Table 1 where independent values for each of the sub-regions are estimated along with the overall activation energy for the process (the total E_a).

While the method applied here is not commonly pursued during traditional kinetic studies, it is felt this approach, as illustrated in Figures 4 and 5 and Table 1, provided good results for E_a at the expense of accuracy in the value for A . These parameters have been determined by a number of authors over the years. A couple of those can be noted here. Using TGA methods at various heating rates up to 160°C/min, Moore, Tant and Henderson^[6] determined an overall activation energy of 269 kJ/mol on phenolic ablative materials. Also, applying a rate of 1°C/min in air and using three different kinetic models, Ninan^[7] estimated values of 77.7, 81.2 and 102.8 kJ/mol for the E_a of glass/phenolic ablatives.

Table 1. Results from linear tangent analysis of TGA data for Borden resol over three sub-regions within the decomposition process.

	A	E_a
Sub-Region A	$3.68 \times 10^2 \text{ sec}^{-1}$	78.8 kJ mol⁻¹
Sub-Region B	$2.91 \times 10^1 \text{ sec}^{-1}$	68.7 kJ mol⁻¹
Sub-Region C	$6.98 \times 10^3 \text{ sec}^{-1}$	105.8 kJ mol⁻¹
Overall		253.3 kJ mol⁻¹

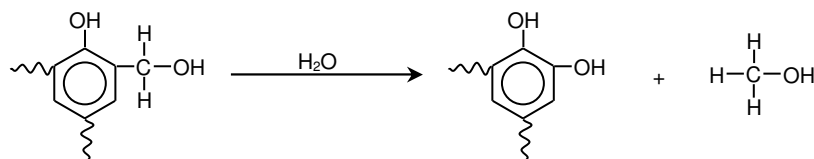
In a study by Chang and Tackett^[4], samples of cured phenolic resin were subjected to TGA-MS in efforts to characterize the material throughout the decomposition process. One of the most interesting results from this study was the analysis of pyrolysis gases released while the polymer was heated to about 1400°F at a rate of 40°/min in He resulting in a 50% char yield. For this current paper, we have taken some of their results (TGA weight loss data and MS trace ion curves) and formulated a new table to contain, not only the compound weights detected and corresponding peak temperatures, but also the estimated molecular fractions and temperatures pertaining to the apparent start of weight loss for each compound detected. These results with a few notes are given in Table 2 below.

Table 2. TGA-MS results for cured phenolic resin samples showing pyrolysis/oxidation gases released during TGA heating to 1400°F at 40°F/min in He . Data extracted and modified from study by Chang and Tackett.

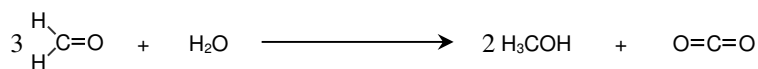
	50% of TGA Weight Loss %	Estimated Mole Fraction %	Peak Temperature °F	Start Temperature °F	Comments and Notes
water	0.8	2.49	248°	-----	peaks & start points coincide
phenol	0.3	0.18	293°	-----	
water	4.4	13.7	410°	338°	
phenol	1.8	1.07	410°	338°	
methanol	1.2	2.10	410°	338°	
carbon dioxide	0.4	0.51	410°	338°	
ammonia	2.7	8.91	518°	410°	peaks & start points coincide
unidentified	0.3	0.42	734°	653°	
water	5.0	15.6	824°	698°	peaks & start points coincide
carbon dioxide	0.7	0.89	824°	698°	
water	5.7	17.8	1148°	995°	peaks & start points coincide
carbon dioxide	1.3	1.66	1148°	995°	
methane	3.8	13.3	1238°	986°	peaks only coincide
benzene	3.4	2.44	1238°	824°	
toluene	2.7	1.61	1220°	932°	methane emitted to 1400°
xylene	1.3	0.69	1211°	986°	
trimethyl benzene	0.2	0.09	1202°	-----	peaks & start points coincide
phenol	4.1	2.45	1292°	806°	
cresol (methyl phenol)	2.6	1.35	1292°	806°	
dimethyl phenol	1.1	0.51	1328°	-----	
trimethyl phenol	0.1	0.04	1328°	-----	rapid drop after peak
carbon monoxide	6.1	12.2	1382°	990°	

50.0 100.0

Consider the components detected up to about 650°-700°F. First, it is believed that the production of water up to this temperature range is primarily a result of continued curing and advanced condensation reactions within the phenolic network leading to additional crosslinking and the release of 'residual volatiles'. However, water is also produced during the early degradation phase when oxidation/combustion reactions take place, as will be indicated later. Smaller molecules, such as phenol and methanol are hydrogen bound until the thermal energy allows their expulsion. Free phenol is released from the resin and immediately volatilizes as do trapped moisture, CO₂ and methanol. The presence of methanol in the resin solution could be due to earlier reactions involving hydrolysis of unreacted methoxy groups within the polymer adduct . . .



or simply by hydrolysis of free formaldehyde with the production of CO₂ . . .



Amine-based compounds are common catalysts in phenolic resin systems. At high enough temperatures, unreacted portions of these catalysts will begin to break down releasing ammonia. Other resin components might include trace amounts of activators (metal chelates for instance), oxidation inhibitors or perhaps wetting agents. Beyond about 700°F, degradation of the organic network commences and the polymer phase begins to lose its identity.

It should be noted that MS will not detect anything below about 10 MW units, thus hydrogen, which we know is generated during the carbonization process, is not indicated at all in these results. Studies by other workers utilizing chromatography techniques have demonstrated elemental hydrogen to be a major pyrolysis constituent. For instance, using other techniques in addition to MS, such as Gas Chromatography (GC), Thoeni, Baker and Smith^[8] reported a hydrogen emission level of approximately 25% of the total TGA weight loss for samples of urethane-furfuryl polymer, in addition to the expected pyrolysis/oxidation products emitted, ie... CO₂, CO, methane and monomeric derivatives of the polymer tested. Table 3 is a duplication of their results and reveals that a portion of the hydrogen was released in the 700°-1200°F range while most was detected at higher temperatures.

Table 3. TGA-GC results for urethane-furfuryl alcohol samples evaluated by Thoeni, Baker and Smith indicating decomposition gases evolve. Of particular interest here is the hydrogen generated during the process.

	Quantity Volatilized (in cm ³ /g of initial sample)			
	80 - 400°F	400 - 730°F	730 - 1255°F	1255 - 1920°F
carbon dioxide	4.5	27	10	2.1
carbon monoxide	0.016	1.8	20	8
hydrogen	-----	-----	28	75
methane	-----	0.42	28	4.5
hydrogen cyanide	0.01	0.01	0.13	1.3
furan	0.05	0.04	0.2	0.02
tetrahydrofuran	0.2	0.4	0.9	1.8
light hydrocarbons	0.12	0.3	4.2	3.7

To avoid confusion with our current study, note that the appearance of cyanide and furan in Table 3 are reflective of the particular polymer these researchers investigated – Table 3 provides its benefit by demonstrating that, with little doubt, hydrogen is a major player in the decomposition process, especially at higher temperatures. A thorough analysis of the decomposition gases would require both MS and GC.

Without information such as that reported in these two studies, a meaningful understanding of the decomposition process is rather vague. Our objective now is to identify and formulate likely carbonization mechanisms and reaction pathways by accounting for some of the major components listed in Table 2 during the decomposition phase (that is, after about 700°F) in conjunction with the production of hydrogen and solid char. This analysis will be developed over the next few sections.

Sequence of Bond Cleavage and Free Radical Generation

Thermal degradation of polymers starts with bond-breaking reactions (homolysis) to form free radicals as primary products. In the phenolic macromolecule, there are many different types of bonds and related bond dissociation energies. One might ask, which bonds go first or which bonds represent the weakest links? And just as importantly, at what point does the network transform from an organic polymer into an inorganic char? Undoubtedly, in the distribution of heat throughout the polymer network, some of the stronger bonds will absorb enough energy to rupture while in other areas, some of the weaker bonds

remain intact. Also, it must be realized that in a system continuously increasing in temperature (such as a heating cycle, for instance), the sequence of bond breaking is substantially augmented according to the specific time-temperature profile employed.

For a system comprised of a several types of bonds, a good indicator of relative bond strengths can be inferred by the energies of the specific free radicals generated during the homolysis step. Generally, each cleavage within the structure will produce two radicals, and the more stable the radicals, the more likely the reaction. Basic energetics teaches that the ease of formation of free radicals follows directly with their stability. Recall for instance, benzyl radicals are more stable than alkyl radicals. The familiar inequality expressions given in elementary organic textbooks may help serve as a reminder for a few of the more common radicals . . .

Stability of Free Radical = Ease of Formation =

benzyl > allyl > tertiary > secondary > primary > methyl > vinyl

However, these do not include all the radical forms that must be considered for the phenolic network. Also, the phenolic structure is strongly centered around aromatic functionality, not aliphatic character. Generally, the more carbon atoms there are surrounding the lone electron, the more stable the radical. Conversely, the greater the electron density near the lone electron, the lower the stability of the radical. When electron spin is allowed to delocalize across the molecule (via resonance or conjugation), the more stable the radical becomes.

There are many handbooks and databases available which provide a multitude of theoretical and experimental values for bond strengths as well as enthalpies of formation for a variety of free radicals and molecular pre-cursors. Also, in more recent years, many researchers have determined the energies for a large number of relevant compounds. Unfortunately, most of these bond energy values pertain to smaller molecules, not oligomers or polymer fragments. They are not very representative of the same bond types in larger molecules. This is due to localized conformational stresses and tertiary/quaternary effects within macromolecules and strained polymer segments that are not present in smaller molecules. However, since this type of data is the only indication of bond strengths readily available, we will make the best possible use of it for comparing and ranking the relative bond dissociation energies present in the cured phenolic resin structure. A closer examination of the proposed structure given in Figure 1 is in order here and is replicated in Figure 8 below. Let us consider the various radicals that might form during thermal cleavage of some of the most important links in the phenolic network.

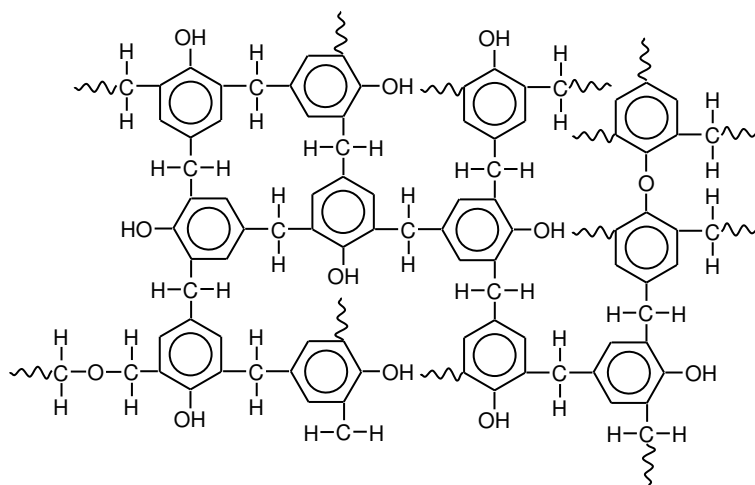
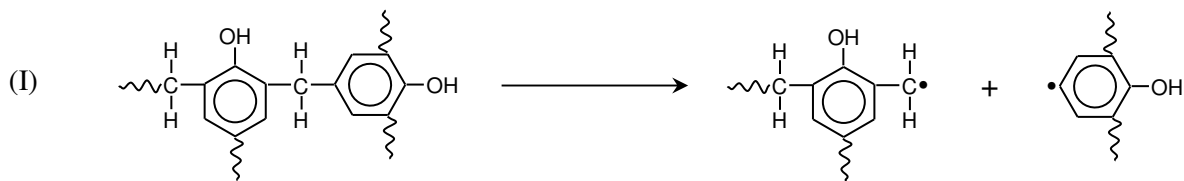


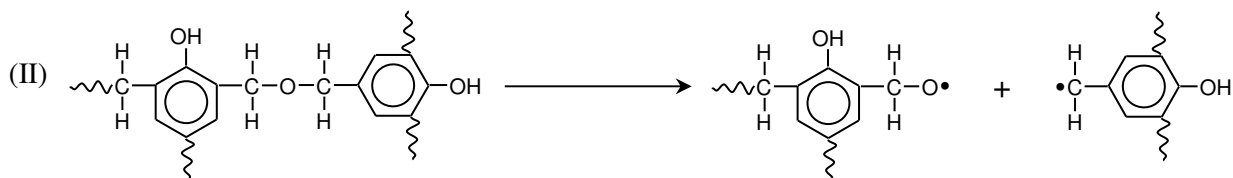
Figure 8. Suggested representation of an idealized cured phenolic resin structure.

» Cleavage of a methylene link to form a benzyl radical and a phenyl radical . . .



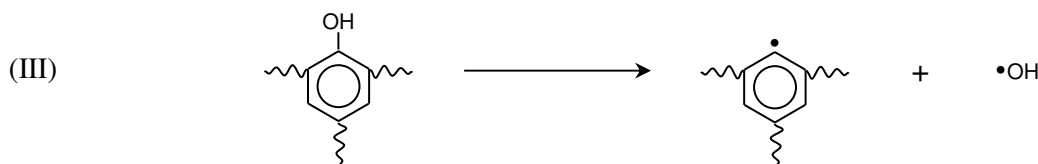
While benzyl radicals are known to be very stable, phenyl radicals are not as much so. The bond dissociation enthalpy for the same methylene link in diphenyl methane, $Ph-CH_2-Ph$ has been determined by a number of workers^{[9][10][11]}: 405.8, 333.0, 343.1, 348.9, 354.8, 374.9 and 367.4 kJ/mol with an average of 361 kJ/mol. Now the -OH groups and methylene links at all the ortho and para positions will enhance delocalization of the radical electron, so rather than use the average, we choose the lowest of the numbers and presume (just for our study) that the bond dissociation energy for the methylene link is approximately equal to 333 kJ/mol. Also, as we shall see, both of these radicals undergo rearrangements to produce even more stable radicals as pyrolysis/combustion commences.

» Cleavage of a methoxy link to form a benzoyl radical and a benzyl radical . . .



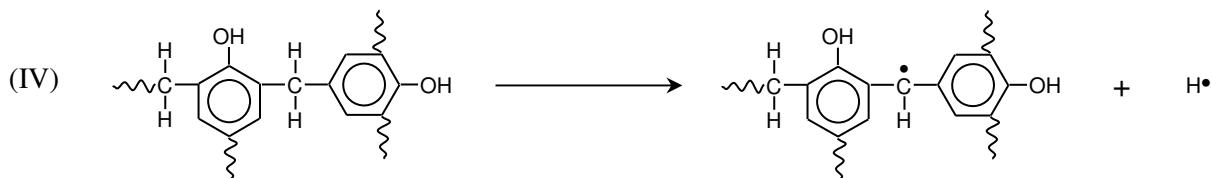
Both of these radicals are highly stable and the presence of methylene links on the benzoyl radical enhances the radical even further. The bond strength of this link is expected to be relatively low. The only dissociation energy data that could be obtained with any similarity to this structure was the Handbook value for the methyl-benzoyl link^[12] CH_3-O-Ph , which is given as 280.3 kJ/mol. The occasional phenoxy-to-phenyl link that forms in the structure $Ph-O-Ph$, can also be considered to rupture at or before this level of energy is reached.

» Cleavage of a hydroxyl link to form a phenyl radical and a hydroxyl radical . . .



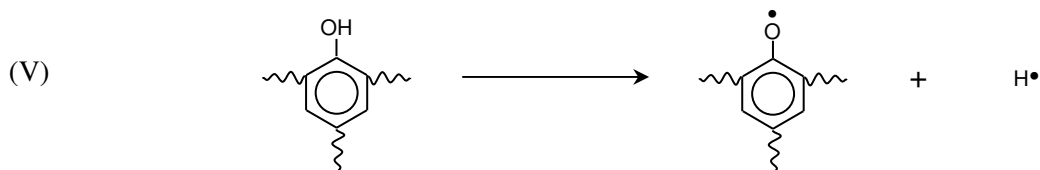
The bond dissociation enthalpy for simple phenol has been documented at 470.3 kJ/mol^[9]. Given the resonance stabilization associated with these structures, this value should probably be notably lower, but for brevity, 470 kJ/mol is assumed (for this study) to represent the energy required to abstract an -OH group from the phenolic structure.

» Cleavage of a methylene hydrogen to form a diphenyl methyl radical . . .



Here, the polymer backbone is not actually ruptured but at some point, stripping of hydrogens in the network must be considered. Recall that the ease of abstraction of hydrogen atoms follows the same priority as that for free radical formation. Thus, the benzylic hydrogen should be relatively easy to abstract. The methylene carbon-to-hydrogen bond energy for diphenyl methane has been experimentally determined and estimated^[13], 340.6 and 334.1 kJ/mol respectively. Again, due to the unusual stability with this configuration (relative to diphenyl methane), 334 kJ/mol is momentarily taken as the strength for this bond.

» Cleavage of a hydroxyl hydrogen to form a phenoxy radical . . .



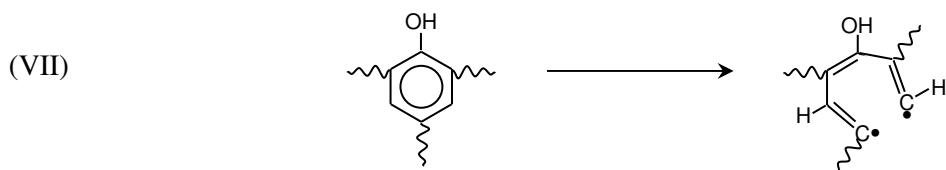
Like benzyl radicals, phenoxy radicals are low in energy as a result of electron delocalization and the availability of several resonating structures. Its bond strength is expected to be relatively low. For simple phenol, the bond dissociation enthalpy for the phenoxy-to-hydrogen link has been determined many times by several researchers^{[9][10][14]}. The average of all these values is 365.3 kJ/mol with a minimum of 331.8 and maximum of 401.7 kJ/mol. For this study, its value will be taken as 331 kJ/mol.

» Cleavage of primary phenyl hydrogens to form phenyl radicals . . .



A number of authors have determined the bond dissociation energy for abstraction of hydrogen from the benzene ring^{[9][10][15]}. The average of all these values is 476.0 kJ/mol with a maximum of 474 and a minimum of 463 kJ/mol.

» Cleavage of an aromatic ring to produce a linear diradical . . .



Cleavage of the basic phenyl structure is a ring opening process. The segment momentarily maintains conjugation, but becomes aliphatic as aromaticity is lost. While this bond strength is often estimated from aliphatic counterparts, there is no way to actually measure the aromatic resonance energy. One textbook source was identified and stated the measured the carbon-carbon net bond energy for simple benzene to be 518 kJ/mol^[16] while the Handbook value gave 488 kJ/mol^[12]. The average of these two is 503 kJ/mol.

While there are surely other bonds that must be broken as the structure decomposes, these 6 or 7 reactions are relevant possibilities to consider during the initial and intermediate phases of the degradation process. Table 4 gives a summary and ranking of these results for comparative purposes.

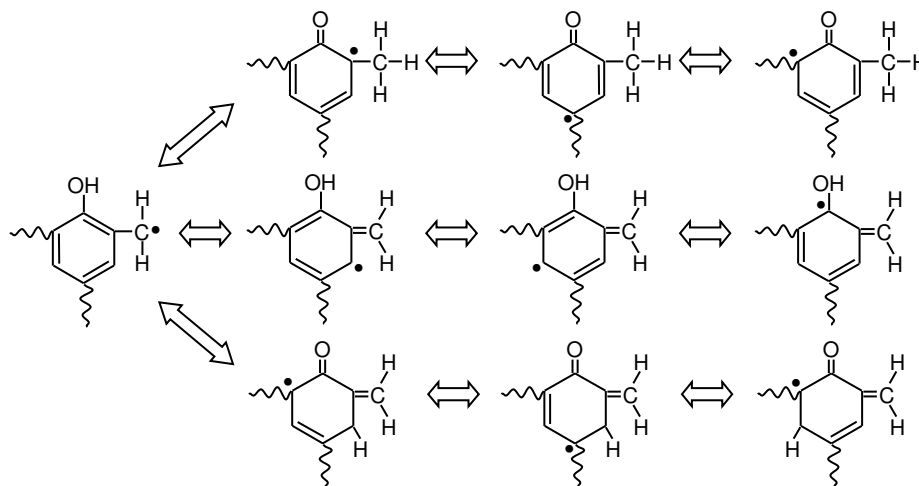
Table 4 . Simplified ranking of relevant bond dissociation energies for the phenolic network.

Bond/Link Description	Formula	kJ/mol
benzyl-benzyloxy (ether) link	$\text{C}_6\text{H}_5\text{CH}_2 - \text{OCH}_2\text{C}_6\text{H}_5$	280
hydrogen-phenoxy link	$\text{H} - \text{OC}_6\text{H}_5$	331
phenyl-methylene link	$\text{C}_6\text{H}_5 - \text{CH}_2\text{C}_6\text{H}_5$	333
hydrogen-methylene link	$\text{C}_6\text{H}_5 - \text{H} - \text{CH} - \text{C}_6\text{H}_5$	334
hydrogen-benzene link	$\text{H} - \text{C}_6\text{H}_5$	463
hydroxy-phenyl link	$\text{OH} - \text{C}_6\text{H}_5$	470
carbon=carbon benzene link	$\sim\text{CH}_2 = \text{CH}_2\sim$	503

It should be emphasized that this over-simplified approach does not necessarily mean the links will rupture in the order given. On the contrary, one scenario might call for phenyl rings to remain intact throughout much of the pyrolysis cycle, in which case the associated phenyl hydrogens are not stripped off until late in the process - just before the aromatic carbons are converted into inorganic char. The primary benefit of this ranking exercise was to establish an apparent priority or guideline for bond scission and most importantly, to gain some insight as to which bonds might go first, i.e. . . . the 'weakest links'.

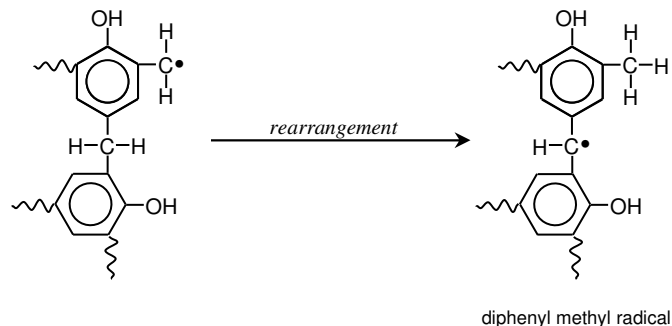
Rearrangements and Early Degradation Reactions

During the early stages of the decomposition process, Eq (I) becomes a very important reaction to take into account. It is suggested here that cleavage of the methylene link forms the basis for the initiation of phenolic matrix degradation. The ease of formation for the radicals generated in this step (and hence, the likelihood of Eq (I) occurring) can be supported by considering some of the resonance structures (equivalent rearrangements) available to these molecular fragments. Consider the possible resonance forms for the benzyl (or phenyl methyl) radical given in Eq (I) . . .



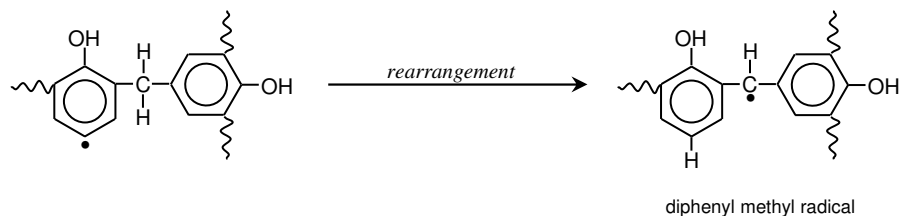
With so many available configurations to accommodate (delocalize) the radical electron here, it is not difficult to see why this radical has a high probability to form. However, consider the likely

rearrangement that surely occurs when the lone electron is shifted inward to form the even more stable dibenzyl (or diphenyl methyl) radical . . .

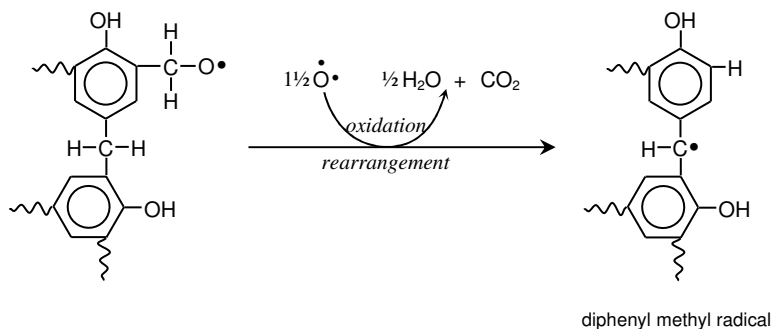


We shall not attempt to draw all the possible rearrangements for the diphenyl methyl radical here. Suffice it to say that, compared to the phenyl methyl radical, the number of resonance structures for this configuration is vast considering the fact that the lone electron now has at least two rings to spread over. This diphenyl methyl radical bears substantial similarity to the famous triphenyl methyl radical which is one of the most stable (and long-lived) radicals ever to be discovered. Interactions between di- and tri-phenyl methyl radicals are significant during the carbonization process and will be treated shortly. For the present however, it is suggested here that this species, *the diphenylmethyl radical is the primary propagating radical in the decomposition of phenolic networks*.

Look again at Eq (I). The not-so-stable phenyl radical now has an opportunity to rearrange itself . . .



Consider Eq (II) in which a benzoxy radical is generated. In the presence of a little oxygen (early in the decomposition process), rearrangement might bring about the following reaction in which CO_2 and water are produced . . .



Where $\dot{\text{O}}$ represents an oxygen atom or radical (oxygen is considered to be dissociated before entering the reaction process). It is suggested here that, for relatively slow heating rates ($< 500^\circ\text{C}/\text{min}$)

oxidation/combustion reactions tend to dominate the first portion of the overall degradation process and trickle off as pyrolytic reactions begin to take over. Using similar approaches, one can validate that reactions (III) through (VI) also lead (predominantly) to formation of the diphenyl radical with side reactions producing the components for water.

Decomposition Pathways and Char Production – Fate of the Diphenylmethyl Radical

Although ring cleavage via Eq (VII) is believed to be a player in the decomposition process, complete destruction of the aromatic structure would produce a mixture of aliphatics. According to Table 2, methane was the only aliphatic compound detected, and this tends to indicate that: (1) phenyl rings are not generally disintegrated since this would likely lead to the formation, at least in trace amounts, of ethane, ethylene, propylene, etc..., and (2) methylene links are degraded, at least to a degree reflective of the fractional amount given in Table 2, which is relatively significant.

It is contended here that one of the primary reaction scenarios likely responsible for generating some of the observed gaseous products as well as char involves consolidation of neighboring phenyl rings, or ring fusion. Consider the following proposed pathways describing possible reactions involving the diphenylmethyl radical and leading to ring fusion under both pyrolytic (anaerobic) and oxidative conditions. First, pyrolysis of the diphenylmethyl radical is expected to give off methane and carbon monoxide, as well as form the precursor to char product, that is, fused ring segments . . .

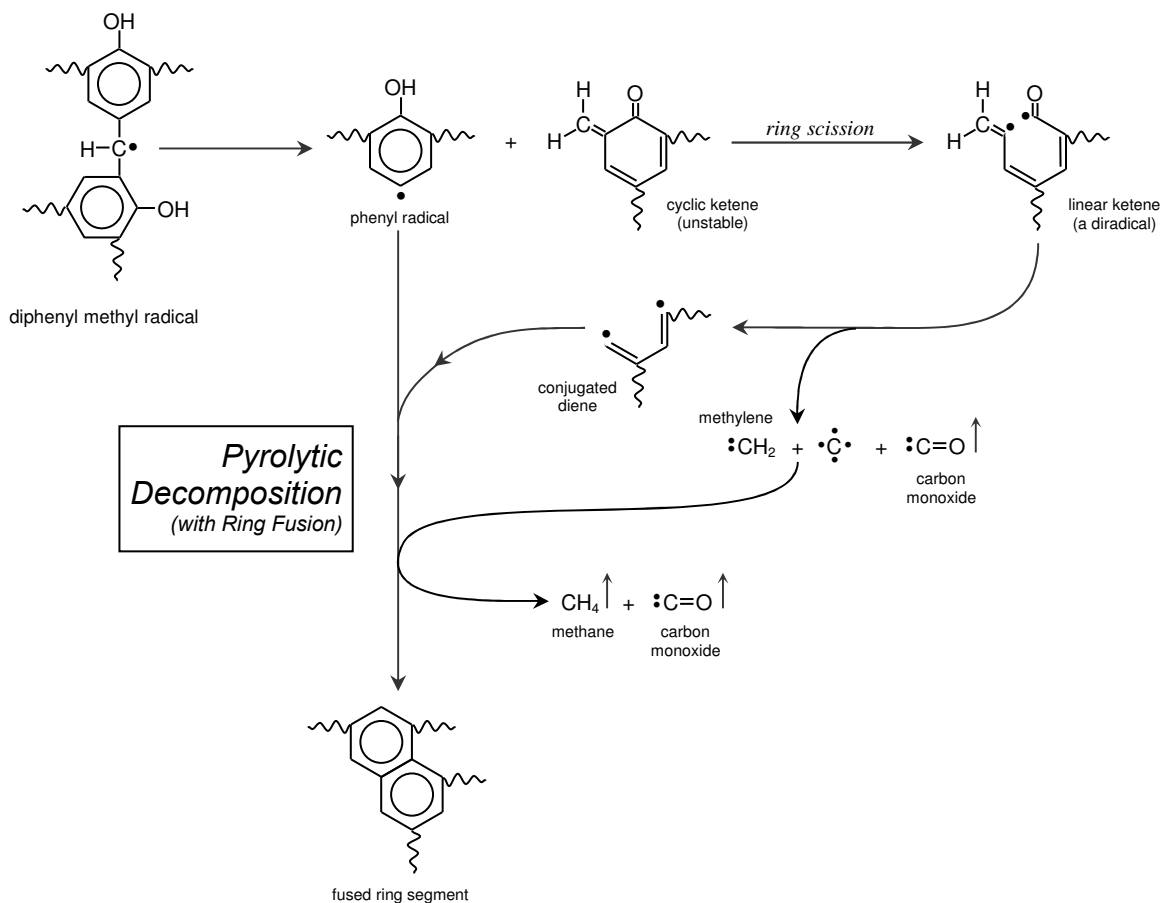


Figure 8. Schematic representation of a suggested pyrolytic reaction path that might take place during the formation of pyrolysis volatiles and char precursor based on consolidation or fusion of neighboring phenyl rings.

As heat is continually added to the system, the formation of less stable radicals becomes feasible. Here, the phenyl radical (step one) is presumed to survive long enough (without rearranging) to enter into the pyrolytic ring consolidation process illustrated in Figure 8. Formation of the unstable ketene intermediate leads to ring cleavage which results in the production of methane, carbon monoxide and sp^2 polynuclear aromatic domains.

Consider now an analogous scheme in which oxygen is locally available so combustion and partial oxidative reactions can take place. It is presumed that the process environment is conducive to molecular bond scission so that oxygen (atomic) radicals are readily available as strong oxidizing agents. Now oxidation is more complex than pyrolysis since some products may be fully oxidized and others only partially oxidized. For instance . . .

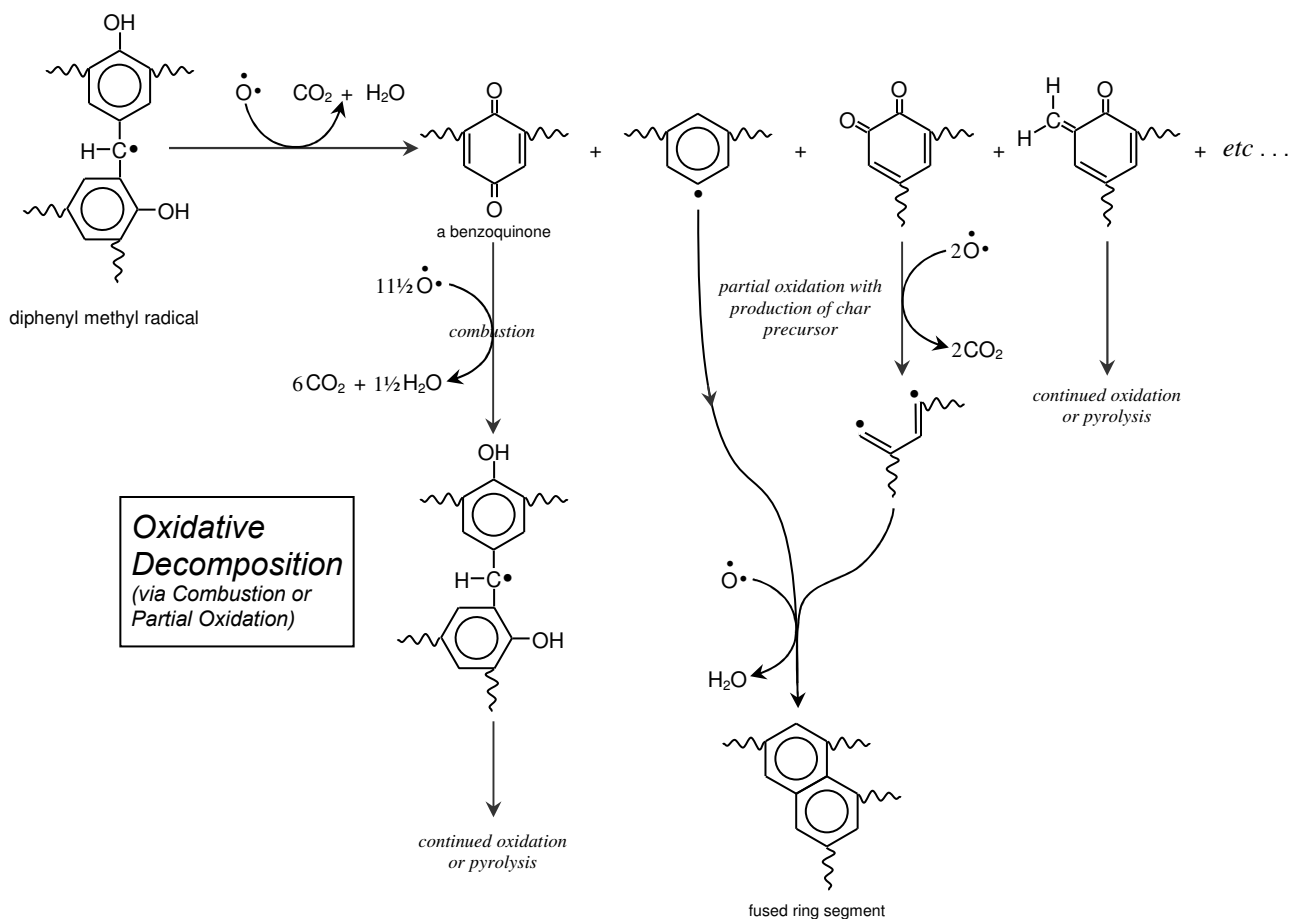


Figure 9. Schematic representation of a suggested oxidation and combustion reactions that might occur leading to the generation of pyrolysis volatiles and oxidation products with the possible formation of char precursor .

Continuation of the first reaction (oxidation of the quinone) would produce smaller and smaller fragments as the substrate underwent combustion. Note that certain reactions involving oxidation can lead to char production. This series of reactions illustrates the point that it is sometimes difficult to tell the difference between partial oxidation and pyrolysis. In general, oxidation results in the formation of combustion products (CO_2 and water) while pyrolysis generates CO , hydrocarbons and char. Aggressive or full oxidation should disintegrate most of the char formed in the process. Both pyrolytic and oxidative decomposition make use of Eq (VII).

Now if the fusion of phenyl rings was the only or even primary mechanism leading to char formation, the system would probably pass through mesophase and then graphitize. Also, if ring fusion within any given fragment is too extensive, then mesophase formation becomes possible. We know this does not occur. Ring consolidations within fragments that remain highly networked with aliphatic (methylene) crosslinks should not pass through mesophase. As a matter of fact, it has been revealed many times by direct experience that the production of glassy, non-graphitic char from cured phenolic resin is exclusively a solid state process – the formation of liquid or semi-liquid components has never been observed. Processes leading to ring fusion can only be considered as secondary pathways to solid state char production. On the other hand, a complete breakdown of the entire methylene link network would be contrary to the confirmed structure of phenolic-based glassy carbon substrates which are known to retain a substantial resemblance to the original organic crosslinked polymer network, just as other glassy chars have been shown to resemble their specific precursors.

One of the most important phases of the decomposition process involves the removal or abstraction of hydrogen from the network. Due to the relative bond energies, dehydrogenation is expected to extract the aliphatic (methylene) hydrogen atoms before affecting the aromatic rings. Consider another reaction involving the diphenylmethyl radical . . .

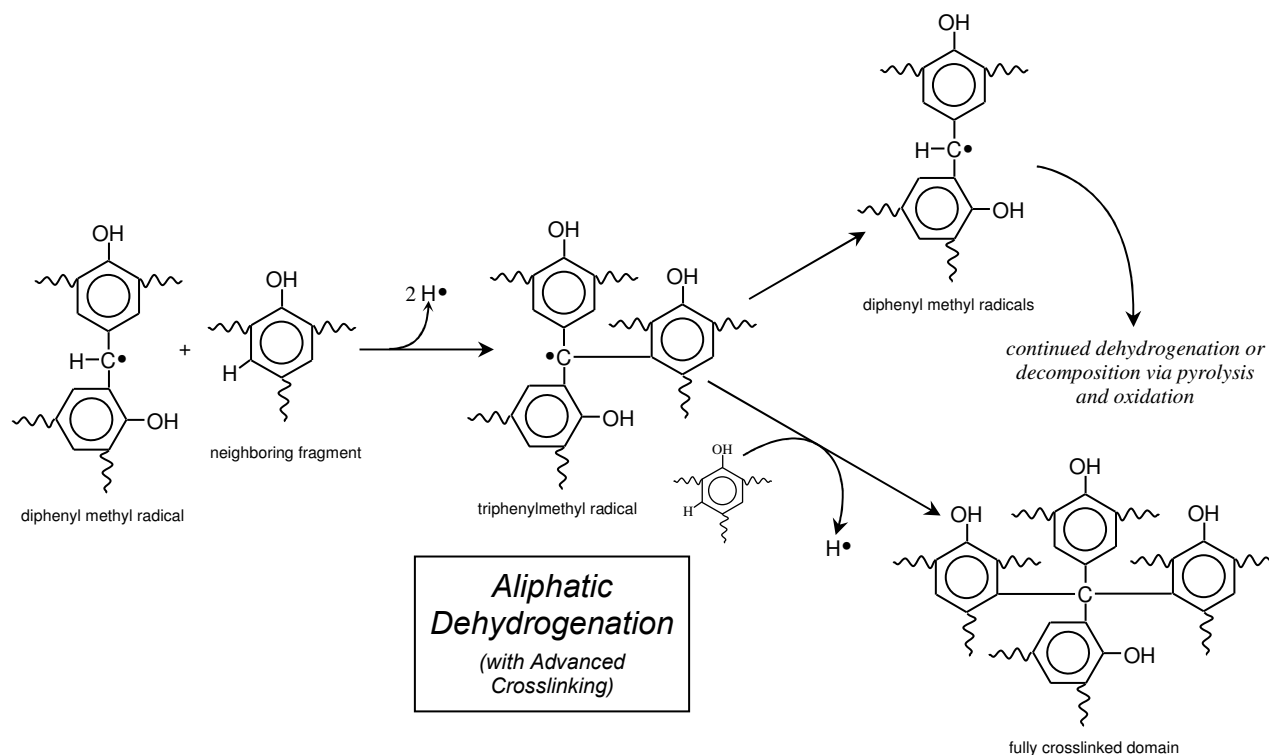


Figure 10. Schematic representation of suggested crosslinking reactions that most likely occur during the formation of rigid carbonized phenolic char in competition with and/or complimentary to ring consolidation reactions.

This scheme is an extension of Eq (IV). Here, it is entirely possible that the appearance of the diphenylmethyl *di*-radical is an intermediary to production of the triphenylmethyl radical. Formation of the extremely stable triphenylmethyl radical is very likely and affords the opportunity to either develop advanced

crosslinks with available sites on neighboring phenyl rings or continue along pathways of pyrolysis/oxidation similar to those outlined in Figures 8 and 9. It is also obvious that neighboring di- and tri-methyl substituted phenyl rings will strongly direct ortho/para substitution during crosslink formation (that is, ortho/para relative to the methylene groups). The aliphatic hydrogen atoms generated here can combine and flow out of the system (to the GC detector for instance) or they may interact with other reactions taking place in the network (such as erosion). The additional crosslinks established in this part of the process are believed to enhance the already rigid crosslinked network that is reflective of the original organic phase. Obviously, formation of these links will be governed by steric hindrance factors and the local availability of phenyl reaction sites to methylene carbons (since all four methylene bonds become equivalently 'saturated', after this point, it may be more appropriate to consider them as methyl groups). It is believed that a majority of saturated aliphatic crosslinks are established before the higher energy aromatic hydrogens are affected.

While crosslinking contributes little, if any, to volumetric shrinkage of the substrate, it is believed that the majority of contraction comes about as a result of (1) ring consolidation or fusion, (2) erosion of polymer end groups resulting in the release of low molecular weight organic compounds, and (3) abstraction of hydrogen (dehydrogenation). Examples of reactions responsible for generating pyrolysis gases, including pyrolytic methane and CO, as well as the major oxidation products CO₂ and water, have already been outlined, and are believed to contribute to the observed substrate weight losses occurring during the decomposition process. In addition however, it is suggested that bond rupture and degradation of peripheral polymer groups begins to occur releasing various amounts of benzene and phenol along with various fractions of their methyl derivatives. It is suspected that these compounds are due to pyrolytic (anaerobic) scission reactions which result in de-linking and partial stripping of terminal rings located near polymer ends across and within the surfaces of substrate fragments. Hydrogen atoms (radicals) present in the system from crosslinking reactions may facilitate this etching/degradation process. Making use of Eq (I), a simplified illustration might be suggested . . .

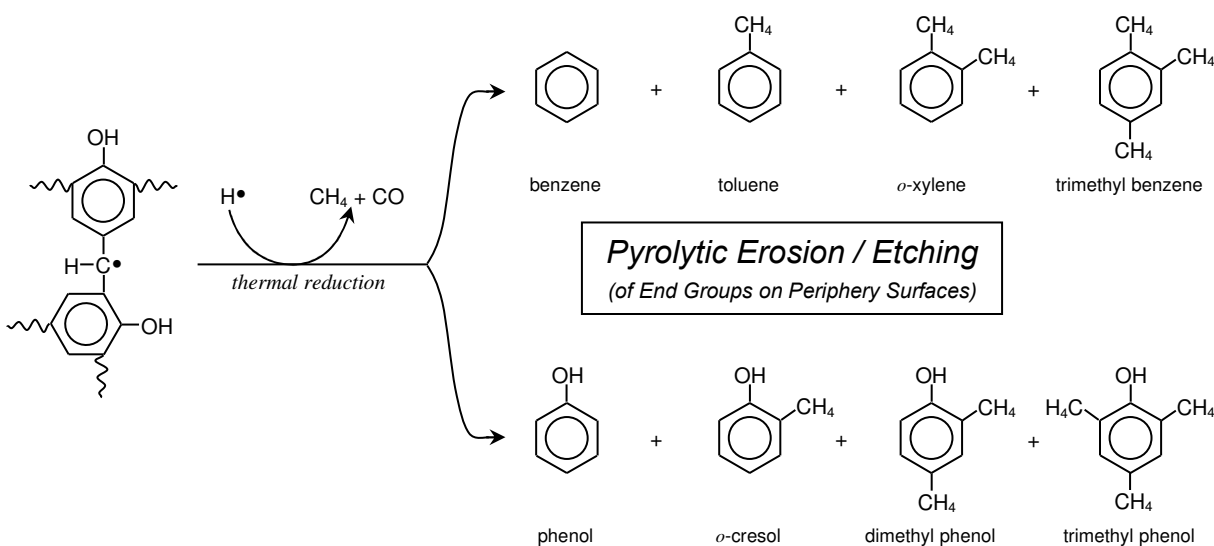


Figure 11. Schematic representation of suggested thermal erosion reactions that could be responsible for generating some of the organic gases released during the decomposition process.

The time-temperature regime where the reactions generating benzene derivatives occur appears to coincide approximately with and essentially overlap those reactions resulting in phenol and its derivatives (Table 2). The slight difference in release temperatures between the aryl rings and phenol rings may be due to residual hydrogen bonding effects between phenol groups. In both cases, it is suggested that these erosion reactions, take place predominantly across the open peripheral surfaces, internal pore surfaces, pore

edges, openings, cracks and crevices resulting in general contraction (or volume loss) of the substrate accompanied by overall pore enlargement. This process can be defined appropriately as a form of pyrolytic etching or thermochemical erosion and is believed to be one of the primary pathways contributing to substrate weight loss during pyrolytic heating cycles and TGA tests.

Under ordinary (room) conditions, abstraction of hydroxy groups from the phenol ring is quite difficult. However, due to the elevated and increasing temperatures, production of less stable radicals is feasible and higher energy reactions become likely. Another reaction which must occur and contributes to substrate weight loss as well as volumetric contraction and production of CO is the abstraction and destruction of phenol hydroxy groups. Available methylene links and carbon radicals generated from other processes can facilitate the dehydroxylation reaction. A simplified version of the reaction might be illustrated by . . .

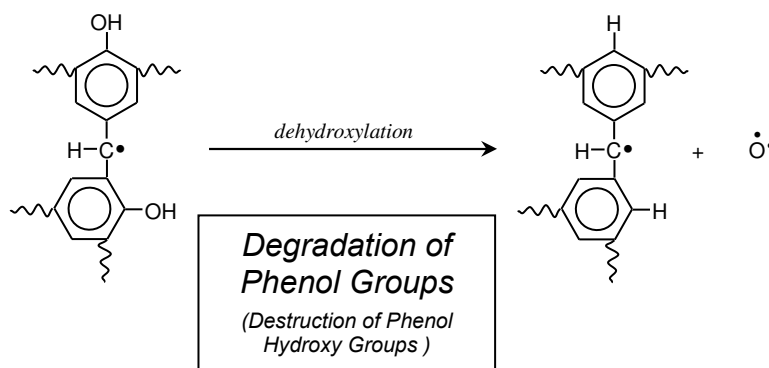


Figure 12. Possible scheme showing likely reaction for removal and disintegration of residual phenol hydroxy groups.

This is an extension of Eq (III). Considering the vast number of phenol rings present in the original system, the effects of this reaction could be relatively substantial. Oxygen radicals generated here can (1) initiate or enhance oxidative degradation (Figure 9), and/or (2) steal carbon atoms from pyrolytic degradation reactions and produce CO (Figure 8).

Now let us attempt to account for and rank the contributing processes and associated gases responsible for substrate weight loss during the decomposition of phenolic resin . . .

- (1) Pyrolytic etching/erosion of polymer end groups to produce methane, CO and aromatic derivatives.
- (2) Dehydrogenation of aliphatic and aromatic hydrogens to form molecular hydrogen.
- (3) Pyrolytic decomposition via ring cleavage with the release of methane and CO.
- (4) Oxidative degradation via ring destruction (combustion) generating CO₂ and water.
- (5) Abstraction and destruction of residual phenol hydroxy groups to produce reactive oxygen.

Obviously, the relative ranking of (3) and (4) is dependent on the level of available oxygen sources in the system. One may speculate on the fate of all these gases immediately after their production. Obviously, pyrolysis gases generated along surfaces are easily carried out of the system, almost instantly. However, gas molecules formed in the interior of the substrate must diffuse out of the confines of the micro-structure, rather rapidly. The full ramifications for rapid mass transport of these interior gases out of the system is not completely understood. It is suggested that diffusion of all the gaseous species generated throughout the decomposition process creates a sub-network of micro-porosity which interconnects with the larger pore channels to facilitate their removal.

Now it is presumed here that the methylene (or methyl) crosslinked network is essentially established before abstraction of aromatic hydrogens really takes off. In general, dehydrogenation begins sometime after the commencement of oxidation and ring fusion reactions and slowly increases as degradation progresses. Aromatic dehydrogenation comprises the last portion of the decomposition process with abstraction reactions becoming most aggressive up to the point of carbonization. As hydrogen is abstracted, carbonization (phase conversion) of the substrate progresses. Regions across the network transform from the organic phase into inorganic carbon as localized domains of inert char begin to develop and expand. When hydrogen atoms are stripped off from a given molecular segment, all other reactions stop and that segment becomes fixed in space as hard, inorganic carbon. Abstraction of hydrogen marks the transition point from the reactive organic phase to the inert carbon state. From a simplified perspective, the carbonized structure might be visualized as randomly spaced regions or groups of 6 membered sp^2 bonded cyclic structures held tightly within a network of sp^3 crosslinks which prevent structural movement or mesophase formation. A simplified illustration of the carbonized structure might be represented by . . .

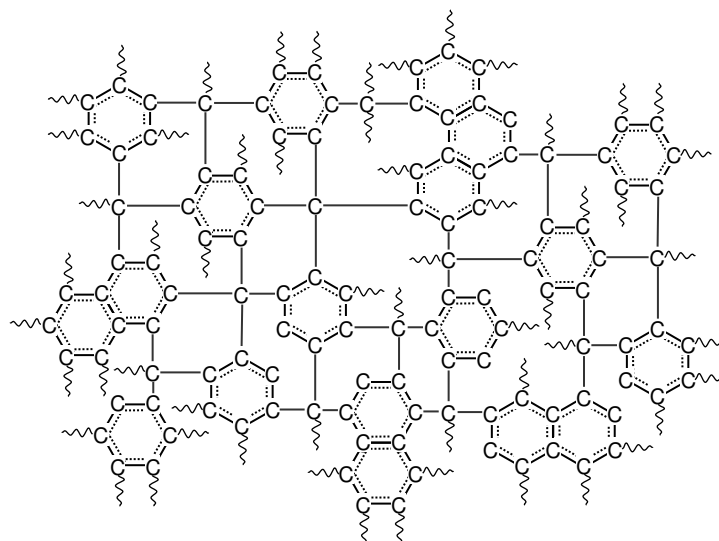


Figure 12. Schematic representation of suggested structure for fully carbonized phenolic resin showing pseudo-hexagonal ring sub-structures embedded within highly crosslinked glassy network.

Here, fully and partially saturated methylene links rigidly suspend a post-aromatic phase consisting of carbon residues of formerly substituted phenol rings and consolidated phenyl rings to form the overall inorganic structure. From a macro-structure perspective, the material would probably be considered as highly isotropic, monolithic and completely amorphous. From a micro-structure perspective, the material is probably anisotropic and multilithic with widely scattered domains of semi-crystalline nature. The chemical structure appears to accommodate both sp^2 bonding (within the hexagonal cyclic groups) and sp^3 bond orbitals (former methylene crosslinks). It would not be too surprising for the solid char to actually exhibit a bit of paramagnetism due to the possible existence of an intermittent free radical phase.

In light of the our discussion, we can now modify the classical free radical inequality and make the following claim pertaining specifically to radicals within the degrading phenolic network . . .

$$\text{Stability of Free Radical} = \text{Ease of Formation} =$$

$$\text{triphenylmethyl} > \text{diphenylmethyl} > \text{benzyl} > \text{phenoxy} > \text{alkyl} > \text{phenyl}$$

Thus, in conclusion, it is proposed here that the process of thermal decomposition of cured phenolic resin subjected to modest testing or firing conditions proceeds through a series of reactions and processes

leading to both simultaneous and independent production of solid state char and pyrolysis gases as outlined in the following statements.

- (1) Random scissions along the methylene crosslink network (or backbone) which evolve into pyrolytic or oxidative pathways representative of those outlined in Figures 8 and 9 with the simultaneous production of char and pyrolysis / combustion gases, CO, CO₂, methane and water.
- (2) Advanced crosslinking between methylene groups and available sites on neighboring phenyl rings brought about by aliphatic dehydrogenation which produces hydrogen and rigid interconnections within and between fragments as represented by the scenario given in Figure 10.
- (3) Pyrolytic erosion/etching of substrate surfaces, including pores and edges, cracks and crevices with the independent production of monomeric-type compounds reflective of the substrate's organic phase according to the representation given in Figure 11.
- (4) Abstraction and destruction of residual phenolic hydroxy groups on phenol rings. Liberated oxygen can promote continued oxidative degradation and/or retard pyrolytic ring consolidation. A potential reaction scheme is given in Figure 12, as well as Figures 9 and 10.
- (5) Abstraction of hydrogen from phenyl rings (aromatic dehydrogenation) causing phase conversion from aromatic organic carbon to inorganic carbon with the production of hydrogen. The level of unoccupied ring sites still holding hydrogen at this point is unknown. This completes the formation of char and the process of carbonization.

It can now be recognized that contributions to substrate weight loss come both from reactions that produce char with gases and reactions that produce only gases. In addition, it is suggested that variable and significant overlaps occur between these five phases of the process even though the indicated sequence is generally followed, on the average. Also, depending on the conditions of carbonization (maximum temperature, heating rate, environment), there inevitably will be some regions that do not undergo all the reactions and decomposition steps, perhaps due to shielding, and these areas may retain some of the original organic character. Final compositions for phenolic char, after heating to zero weight loss, have been reported^{[4][17]}. Many of these results indicate that trace quantities of both hydrogen and oxygen are often present in the final char.

Summary and Conclusions

A survey of bond dissociation enthalpies provides a guideline to further examine likely radicals formed during the phenolic degradation sequence and some of the rearrangements that occur. Initiation and propagation of phenolic decomposition is built around the premise that the most stable radicals form first and drive the carbonization process however, as the temperature inevitably increases, less stable radicals become available which account for many of the decomposition products generated. All indications are that the diphenyl methyl radical is the primary propagating intermediate (reactant) responsible for driving the various reactions throughout each of the decomposition phases. Pyrolytic decomposition is one the carbonization pathways leading to char through the process of benzene ring consolidation with the production of carbon monoxide. While oxidative degradation can lead to some ring fusion, its primary products are those of combustion that is, carbon dioxide and water. Abstraction of aliphatic hydrogen induces advanced crosslinking within the network via formation of the triphenyl methyl radical, big brother to the diphenyl methyl radical. Pyrolytic chemical erosion or etching of polymer ends along substrate surfaces, in cracks, crevices, pore surfaces and openings is believed to be one of the primary pathways leading to the formation of observed methane, benzene/phenol and its derivatives. Destruction of phenol hydroxy groups

(dehydroxylation) is expected to contribute to weight loss and latent oxidation of the network and may possibly exhibit a slight pyrolysis inhibitor effect. Abstraction and removal of aromatic hydrogen from the system marks the transition point from the reactive organic phase to the inert carbon state. Overall, the system of reactions that makes up the total decomposition process includes reactions that produce both char and gases, reactions that produce char only and those that only form gases. Thus, the decomposition scenario proposed here seems to account for all the gases detected, produces an abundant amount of char and supports findings by other workers which indicate the possible presence of both crystalline-like structure (sp^2 bonding) and amorphous character (sp^3 bonding). It is suggested that the inorganic macro-structure is comprised of hexagonal rings (which may exhibit some sort of inherent resonance) suspended or fixed within a rigid amorphous-like network. This is the basic description of the unusual carbon form referred to as glassy or vitreous carbon which is the solid reaction product of carbonized phenolic resin.

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