

A Kinetic Study of the Oxidative Degradation of Phenol-Formaldehyde Polycondensates Using Infrared Spectroscopy^{*,†}

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In a previous paper,¹ the oxidative degradation of phenolic resin systems was investigated in some detail and a working postulation concerning the primary and secondary oxidation reactions was formulated. During the course of this investigation it became evident that the spectrophotometric method used could be adapted to study the kinetic details of the primary oxidative process and to a degree some knowledge of the relative reaction rate of the secondary oxidative reaction as compared to the primary methylene bridge oxidation could be determined.

It was of interest to determine if any effect on the reaction rate was discernible in resole systems if the phenol-formaldehyde ratio was changed over a broad range and to gain some information regarding the relative reactivities of a carbonyl group in the ortho-ortho position between two phenol rings and a group in the para-para position. If rate differences should occur in these systems when the phenol-formaldehyde (P/F) ratio is changed, added support of the primary oxidation step as proposed in the previous study would be realized. Substantial assistance in the evaluation of further secondary degradation reactions might be gained as well.

Experimental Techniques

Preparation of Resin Samples

The resin samples used in this study were prepared in the following manner. The reactants as summarized in Table I were heated on a steam bath for 2 hr. On cooling, the reaction mixtures were neutralized to pH 7 with 5% aqueous hydrogen chloride solution. The neutralized mixtures were refrigerated for 8 hr. The aqueous layer was decanted off and the

* Presented, in part, at the 138th National American Chemical Society Meeting, New York, Sept. 1960.

† This work was supported in part, under Contract No. DA-30-069-ORD-2626 and Grant No. DS-ORD-31-124-60-G51 from the U. S. Army Research Office, Durham, North Carolina.

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TABLE I
Reactants Used in Resin Preparation

Phenolic component	Wt., g.	Formaldehyde, as 37% aq. soln.	Catalyst, ml. of 4N NaOH	P/F ratio
Phenol	10	10	2	0.83
Phenol	9.40	10	2	0.80
Phenol	10.40	11.70	2	0.77
Phenol	10.10	13.00	2	0.67
Phenol	9.40	14.20	2	0.57
Phenol	9.40	20.20	2	0.40
<i>o</i> -Methylol phenol	12.40	0	2	1.00
Bisphenol A	5	40.00	50	—

viscous liquid polymers washed once with an equal volume of water and again refrigerated. After decantation of the water washings, the polymer was dissolved in acetone and dried over anhydrous magnesium sulfate. After filtration, a clear acetone solution of the phenolic resin was obtained. This solution was used directly for film preparation as previously described.¹

Oxidation Rate Studies

The resin samples were cured in nitrogen at 120°C. for 3 hr. by heating specially constructed curing ovens² under a gas flow of 0.5 CFH. Sample heating was accomplished using a heated cell³ for monitoring the sample at the reaction temperature. The length of heating ranged from 50–500 min. depending on the oxidation rate at the temperature selected. Aging studies in air were carried out at 140, 150, 160, 170, 180, 200, and 220°C. A flow of nitrogen was maintained over the polymer film sample until the desired reaction temperature was attained in order to prevent pre-oxidation. One of the samples was heated at 160 and 180°C. in air, 30% oxygen-70% nitrogen, and pure oxygen. The reaction rates were found to be identical in the 3 sets of aging atmospheres. The spectrum was determined from 5.0–6.75 μ (2000–1500 cm^{-1}) and the absorbance data obtained using the baseline method described by Wright.⁴ The rate data were obtained using the method described by Gugenheim.⁵ This method is especially adaptable for treatment of data of this type since the reactions are pseudo-first-order due to the oxygen excess during the primary oxidation reaction period being studied. A typical set of data is summarized in Table II and graphically plotted in Figure 1.

If times $t_1, t_2, \text{ and } t_3, \dots$ and $t_1 + \Delta t, t_2 + \Delta t, \text{ and } t_3 + \Delta t, \dots$, are selected where Δt is a constant increment, then $(A_t + \Delta_t - A_t)$ can be evaluated where A is the observed absorbance at time t . Then if $\ln(A' - A)$, where A' is the absorbance at time $(t + \Delta t)$, is plotted versus time t , a straight line is obtained whose slope is equal to the rate constant $-K$.

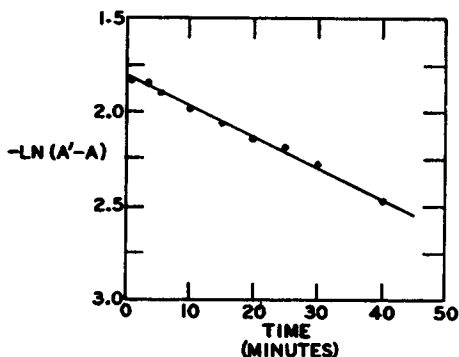


Fig. 1. Data of Table II plotted for the 1650 cm^{-1} band for phenolic resin oxidation at 160°C.

Polarographic Analysis of 2,2'- and 4,4'-Dihydroxybenzophenone

The instrument used in the analysis was a Sargent, model XV, recording polarograph. Polarographic reduction of 2,2'- and 4,4'-dihydroxybenzophenone was carried out according to the following procedure. The composition of the solution was: 30 ml. of 0.1N potassium chloride solution, 30 ml. of acetic acid-sodium acetate buffer solution (pH 4.65), 0.2 g. of gelatin, and 40 ml. of methanol containing 10^{-3} moles of ketone. The solution of 4,4'-dihydroxybenzophenone gave a half-wave potential of -1.27 v., with a small prewave potential curve at -0.98 v. The solution of 2,2'-dihydroxybenzophenone gave a half-wave potential of -1.18 v., with no prewave potential. The two methanolic solutions were irradiated for three days with ultraviolet radiation. These solutions were then reduced polarographically. Irradiated 4,4'-dihydroxybenzophenone gave a curve which clearly indicated three half-wave potentials at -1.27 v., an increased prewave at -0.98 v., and new wave at -0.40 v. Further, reduction of *p*-hy-

TABLE II
Gugenheim's Method Applied to a Phenolic Resin 1650 cm^{-1} Bond In-growth Heated Continuously in Air at 160°C.

Time, min.	A	A'	A' - A	$\text{Ln}(A' - A)$
1	0.005	0.165	0.160	-1.833
3	0.017	0.172	0.155	-1.865
5	0.030	0.180	0.150	-1.897
10	0.060	0.195	0.135	-2.003
15	0.080	0.210	0.130	-2.041
20	0.095	0.215	0.120	-2.121
25	0.110	0.225	0.115	-2.163
30	0.125	0.230	0.105	-2.254
40	0.165	0.240	0.085	-2.466
50	0.195	0.255	0.060	-2.914

droxybenzaldehyde, with a half-wave potential of -1.32 v., showed that this was not one of the irradiated products from 4,4'-dihydroxybenzophenone. No changes occurred upon irradiation of 2,2'-dihydroxybenzophenone. If either ketonic isomer was irradiated as a solid phase film, no changes occurred.

Results and Discussion

The oxidative reaction of the phenolic resins studied was expected to be first order with respect to methylene concentration at the surface of the film samples. From the data obtained on examination of the filmed resin in air, 30% oxygen and 70% nitrogen, and pure oxygen it was apparent that the rate of oxidation was independent of the amount of oxygen over the sample at the concentration levels used in this study. Therefore, a swamp-

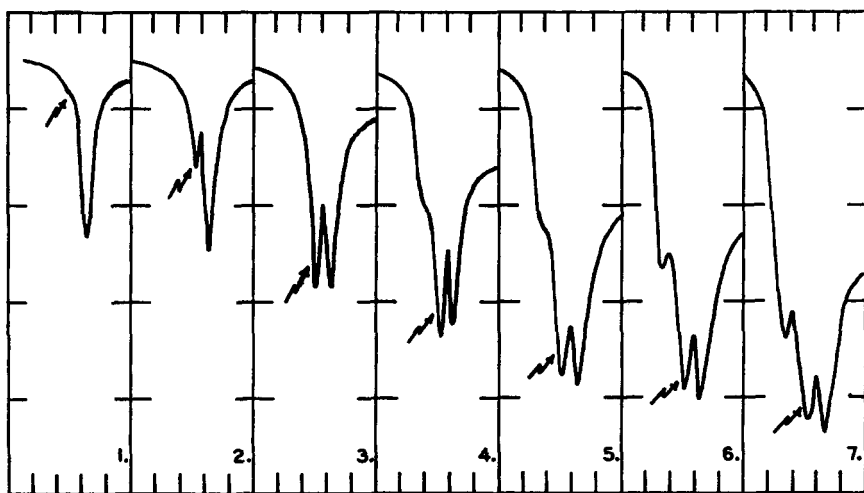


Fig. 2. Representative spectrum between 5.6 and 6.4μ indicating the ingrowth of the 1650 cm.^{-1} band on air oxidation at 180°C . (1) At 0 min. of oxidation, (2) after 2 min., (3) after 12 min. (4) after 25 min., (5) after 100 min. (6) after 175 min. (7) after 300 min.

ing effect of oxygen occurs even in air, and the rate of oxidation is dependent only on the available methylene groups at the polymer surface.

The resin samples were spectrally examined at the reaction temperature through the $5\text{--}6.75\text{-}\mu$ region ($2000\text{--}1500 \text{ cm.}^{-1}$). Data were recorded approximately every 2 to 4 min. over the time interval studied. Figure 2 shows a typical set of curves obtained on oxidation indicating the rate of ingrowth of the 1650-cm.^{-1} carbonyl band. Upon heating in air at 7 different temperatures ($140, 150, 160, 170, 180, 200,$ and 220°C .) absorbance data were obtained for the carbonyl band ingrowth. From these values a plot of carbonyl absorption versus time was constructed for each temperature. These curves are assembled in Figure 3.

If Gugenheim's method⁵ is applied to these data, a series of plots as exemplified in Figure 1 is obtained. At the lower temperatures $140\text{--}160^\circ\text{C}$.,

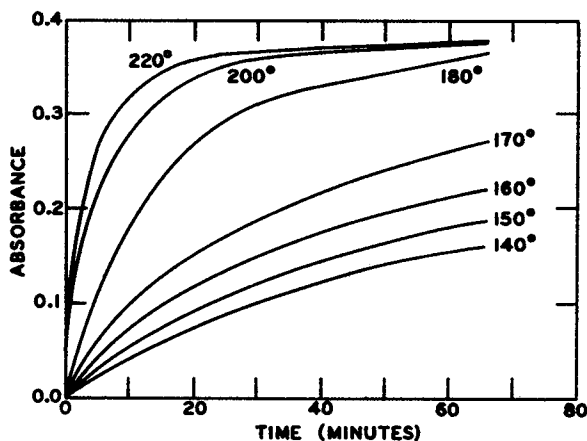


Fig. 3. Typical plots of phenolic resin oxidation expressed as increasing absorbance of the 1650 cm.^{-1} band vs. time at temperatures between 140 and 220°C .

the oxidation is first order with respect to the polymer over the first 50 min. since a straight line plot was obtained. However, at higher temperatures a break in the curve results, yielding essentially two straight lines as shown in Figure 4 for continuous heating at 180°C .

It was first thought that these reactions might not be first order. However, when $\log dA/dt$ was plotted versus $\log A$, a straight line was obtained for values less than 10 min. and whose slope was one, indicating a first-order reaction. There are two possible explanations for a decrease in observed reaction rate after a short period of time at higher temperatures. The first is that all the surface methylene groups are rapidly oxidized and the initial oxidation reaction is slowly choked off since the surface is still almost impermeable to oxygen limiting attack at the inner layers of the system. The second possibility and the most acceptable is that secondary oxidation through the formation of quinoid structures is using up the initial oxidation products in a consecutive reaction sequence, thus decreasing the

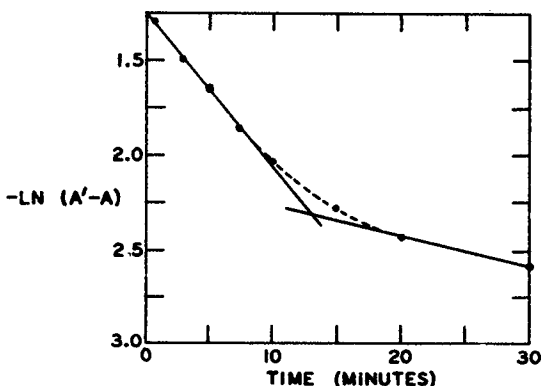


Fig. 4. Data obtained using Gugenheim's method for 180°C . oxidation of phenolic resin.

appearance of the initial oxidation product. Therefore, the most likely reason why no break occurs in the rate curve at 160°C. is that quinoid structure formation is not readily formed at temperatures below 170°C.

The initial rate constant is obtained from the slope of the line at the higher temperatures before the break in the line appears. Table III lists the rate constants obtained by Gugenheim's method.

TABLE III
Rate Constants for the Initial Oxidation Reaction in
Phenolic Resins at Various Temperatures

Temp., °C.	$1/T \times 10^{-3}$ °K.	Rate const.	
		$\times 10^{-2}$ min. ⁻¹	$-\log K$
140	2.42	0.90	2.046
150	2.36	1.40	1.854
160	2.31	2.06	1.686
		2.37	1.625
170	2.25	4.94	1.306
180	2.21	6.88	1.162
		7.67	1.115
200	2.12	17.5	0.757
		17.8	0.750
220	2.03	37.6	0.425

In Figure 5, $-\log k$ is plotted versus the reciprocal of the absolute temperature to give a straight line plot whose slope, when multiplied by 2.303*R* gives an activation energy of 19.5 kcal. This value corresponds favorably with the value for the same oxidation reaction obtained by thermogravimetric methods.⁵

A similar set of calculations based upon the initial oxidation reaction of a series of resins at 160°C. having varying phenol-formaldehyde ratios are shown in Figure 6 in which the rate of oxidation is plotted versus the P/F ratio. Since there is a marked change in the reaction rate when compared with the number of available methylene linkages, the postulates of the primary mode of oxidation as methylene oxidation is firmly established.

To further show the generality of the oxidation phenomena a bisphenol A-formaldehyde polycondensate was examined in a similar fashion. The rate constant obtained was 3.68×10^{-2} min.⁻¹ at 180°C. If this value is compared with that of a phenolic resin of similar preparation at the same temperature (see Table III) it is approximately half that of the phenolic system. This is consistent with the bisphenol A-formaldehyde structure in which the para positions of the phenolic systems are not available for oxidation due to the presence of the geminal-dimethyl group. This further substantiates the postulated initial oxidation reaction.

Furthermore, an insight into the secondary oxidation process can also be gained by a comparison with a phenolic resin system. Since it is postulated that the ingrowth of the band at 1680 cm.⁻¹ (6.2 μ) is a measure of the

quinoid structure prior to chain scission, a comparison of the two systems was made using data obtained at 180°C. The rate constants for quinone-type structure formation was found to be $2.58 \times 10^{-2} \text{ min.}^{-1}$ for the phenolic resin but only $1.48 \times 10^{-2} \text{ min.}^{-1}$ for the bisphenol resin. Once again, the rate is approximately one-half as great in the bisphenol resin. This is in good agreement with the proposed mechanism since the formation of quinoid systems depends on the formation of oxidized methylene linkages.

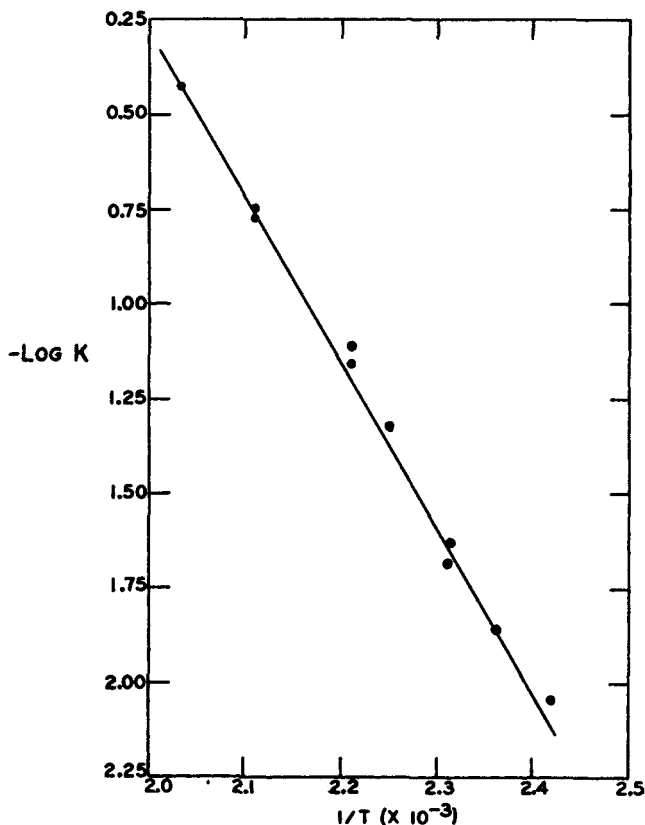


Fig. 5. Graphic representation of the change in rate constant versus the reciprocal of the absolute temperature for estimation of the activation energy of methylene oxidation in phenolic resins.

The third step in the proposed oxidation mechanism is the formation of acid functional groups by further oxidation of the quinoid intermediate. The rate constant was determined by analysis of the ingrowing band at 1720 cm.^{-1} due to acid formation and found to be $5.7 \times 10^{-3} \text{ min.}^{-1}$ at 200°C. Compared to the rate constant for primary oxidation of methylene groups, this reaction is only $1/40$ th as fast. It might be thought that once chain scission occurs and acids are produced, these fragments would volatilize and therefore escape detection. However, this was apparently

not the case in the study since the resin was still present in major quantity as shown by no substantial decrease in the bands in the infrared spectrum. It therefore appears that acid formation is a comparatively slow reaction.

Polarographic Studies of the Reactivity of the Intermediate Ketonic Species

It became of interest to examine any differences which might exist in the ability of the 2,2'- and 4,4'-dihydroxybenzophenone intermediates to react at markedly different rates in the solid phase. As a reactivity test it was decided to study the polarographic reduction of the carbonyl group of the parent ketones after various periods of irradiation with ultraviolet light, since it might be expected that treatment of this type might promote conversion of the ketone to the quinoid intermediate structures. Since

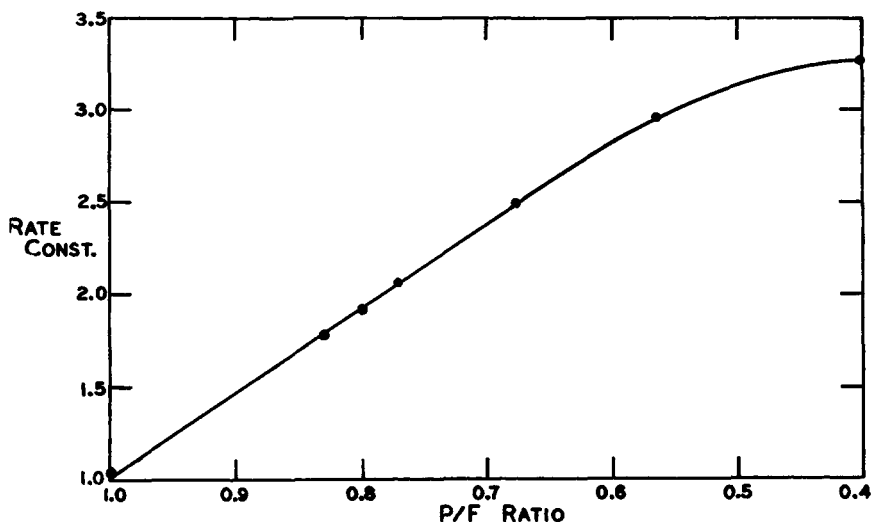


Fig. 6. Effect of changing the resin structure by varying the phenol-formaldehyde ratios as manifested in the rate of oxidation.

each of these species might be expected to be reduced polarographically at different potentials, a qualitative idea as to the reactivity differences between these two species might be gained. As indicated in the experimental section, differences did occur on irradiation in methanol solution. However, solid phase irradiation which is more analogous to the polymer system showed no difference in behavior of these ketones before and after irradiation. At present, it must be assumed, therefore, that quinoid formation at the 2 position or the 4 position is equally facile.

In summary, therefore, a number of occurrences have been detected in the oxidation of phenolic resins. The postulated primary oxidation of methylene linkages to carbonyl intermediates is substantiated on the basis of rate differences exhibited by changing the phenol-formaldehyde ratio in the starting resin. This process is general as shown by the examination of

a bisphenol-formaldehyde polycondensate which exhibited a proportional rate decrease due to fewer available methylene linkages. The formation of quinoid species and their oxidation causing chain scission and acid formation was kinetically examined and is in good agreement with the degradation mechanism. Attempts to polarographically detect differences in reactivity due to the position of the benzophenone linkage and the phenolic hydroxyl indicated that no major observable differences could be detected in the solid phase.

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Synopsis

The oxidative degradation of cured phenolic resin has been investigated by continuous monitoring of the infrared spectral changes occurring in the solid phase at temperatures between 140 and 220°C. The postulated mechanism for oxidation of methylene bridge linkages activated by adjacent phenol rings has been substantiated on the basis of rate differences observed on changing the phenol-formaldehyde ratios. This process is general as shown by a proportional decrease in oxidation on examination of a typical bisphenol-formaldehyde polycondensate. The formation of quinoid species and their oxidation to acid and quinone fragments are in good agreement with the kinetic data and the mechanism proposed earlier. Attempts to polarographically detect differences in reactivity due to the position of the benzophenone linkage and the phenolic hydroxyl indicated that no major observable differences could be observed in the solid phase. The apparent initial activation energy of oxidation is of the order of 19 kcal.

Résumé

La dégradation oxydante de résines phénoliques vulcanisées a été étudiée à l'état solide par l'enregistrement continu des variations du spectre infrarouge au cours du temps à des températures variant de 140 à 220°C. Le mécanisme proposé pour l'oxydation des groupes méthylènes activés par les cycles phénoliques adjacents a été corroboré sur la base des différences de vitesses observées lors de la variation des rapports phénol-formaldéhyde. Ce processus est général comme l'indique la décroissance proportionnelle de l'oxydation pendant l'examen d'un polycondensat bis-phénol-formaldéhyde typique. La formation d'unités quinoniques et leur oxydation en fragments acides et quinoniques correspondent bien aux données cinétiques et au mécanisme proposé antérieurement. Des essais de détection polarographique des différences de réactivité dues à la position du groupe benzophénone et de l'hydroxyle phénolique, indiquent peu de différences observables dans la phase solide. L'énergie d'activation initiale apparente d'oxydation est de l'ordre de 19 kcal.

Zusammenfassung

Der oxydative Abbau von gehärteten Phenolharzen wurde durch kontinuierliche Kontrolle der Veränderungen im Infrarotspektrum der festen Phase bei Temperaturen zwis-

chen 140–220°C untersucht. Der Mechanismus, welcher für die Oxydation von Methyl-
enbrücken bei Aktivierung durch benachbarte Phenolringe angenommen wurde, konnte
auf Grund der Geschwindigkeitsunterschiede bei Veränderung des Phenol-Formaldehyd-
Verhältnisses bestätigt werden. Wie die proportionale Abnahme der Oxydation bei der
Untersuchung eines typischen bis-Phenol-Formaldehyd-Polykondensats zeigt, handelt es
sich dabei um einen recht allgemeinen Vorgang. Die Bildung chinoider Verbindungen
und ihre Oxydation zu Säure- und Chinonbruchstücken stimmt mit den kinetischen Da-
ten und dem früher vorgeschlagenen Mechanismus gut überein. Versuche zur polaro-
graphischen Ermittlung von Reaktivitätsunterschieden als Folge der Stellung der Benzo-
phenonbindung und der phenolischen Hydroxylgruppe zeigten, dass in der festen Phase
keine grösseren Unterschiede beobachtet werden konnten. Die scheinbare Anfangsakti-
vierungsenergie der Oxydation liegt in der Grössenordnung von 19 kcal.

Received October 28, 1961