

Thermal Properties of Resin Copolymers Derived From *o*-Hydroxy Acetophenone

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SYNOPSIS

A variety of crosslinked resin copolymers have been synthesized by condensing *o*-hydroxy acetophenone with formaldehyde and chloro-substituted benzoic acids and anilines in the presence of acidic and basic catalysts. The physico-chemical properties of the resins are reported. The thermogravimetric analysis method was used to study the thermal behaviour of the resins; the evolution of kinetic parameters and degradation mechanism was also investigated. Resins from chlorobenzoic acids showed a clear two-step degradation neglecting moisture loss, whereas those from chloro anilines gave a somewhat continuous sigmoid. The effect of reaction conditions like monomer, molar ratio, and catalyst is also reported.

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INTRODUCTION

Phenol-formaldehyde condensates¹ are materials of great importance² and their synthesis is well documented.³ Over the past decade, an increasing number of investigations in the field have been diverted to develop and analyse thermal stable resins for versatile applicability.⁴⁻⁶ Their use as structural materials for aircraft, however, is limited because of their very low solvent creep, which requires preparation of solvent-resistant polymers. A survey of the literature reveals heat resistant copolymer compositions with benzoic acids and anilines.⁷ More recently preparation and characterization of resins from hydroxy acetophenones have been reported.⁸

The preparation and some physico-chemical properties of resins from *o*-hydroxy acetophenone is presented on this paper. Thermogravimetric (TG) analysis was employed because this dynamic method provides rapid measurement over a wide temperature range and permits information concerning the thermal stability and composition of the original sample, intermediates, and residue.

EXPERIMENTAL

Resins were prepared by refluxing *o*-hydroxy acetophenone (OHAP) with formaldehyde (F) and other comonomers such as chloroanilines (CA), and chloro benzoic acids (CBA), in various molar feed ratios of monomers in the presence of concentrated acids for 5 h and dilute sodium hydroxide for 4 h. The detailed procedure is presented in an earlier communication.⁸ The prepared resins are reported in Tables I and II.

The density of the resins were determined in a small pycnometer at 28°C in dry benzene. Their inherent viscosity was determined with an Ubbelohde viscometer. Solvents used were of Analar grade. IR spectra was recorded with a Perkin-Elmer 781 Spectrophotometer (KBr pellets) TG analysis was carried out with a thermal analyser, 781 series (Stanton-Redcroft, England) in air at a heating rate of 20°C/min.

RESULTS AND DISCUSSION

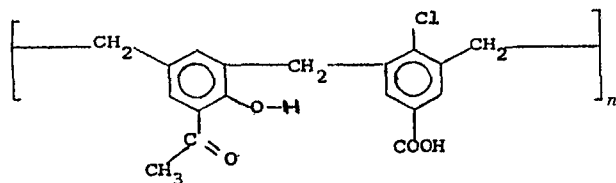
The resin condensates prepared may be assumed to have a novolak type one-one copolymer structure,

Table I Properties of Resins With Chloro Aniline as Comonomer

Sl. No.	Molar Ratio of Monomers OHAP : CA		Catalyst	Substituted Chloro Aniline	Colour/ Structure	Decomposition Temperature (°C)	Density (gm/cm ³)	Inherent Viscosity (dL/g)	Solubility
1	25	75	HCl	<i>Ortho</i>	Orange ^a	320	1.842	1.52	<i>N</i> -butyl amine
				<i>Meta</i>	Orange ^a	320	0.836	1.105	<i>N</i> -butyl amine
				<i>Para</i>	Brick red ^b	300	1.045	1.031	<i>N</i> - <i>N</i> -DMF
2	35	65	HCl	<i>Ortho</i>	Orange ^a	320	1.158	—	<i>N</i> -butyl amine
				<i>Meta</i>	Orange ^a	320	—	1.005	<i>m</i> -Cresol
				<i>Para</i>	Brick red ^b	300	0.775	1.029	Chloroform
3	45	55	HCl	<i>Ortho</i>	Orange ^a	316	1.142	—	<i>N</i> -butyl amine
				<i>Meta</i>	Orange ^a	320	1.394	1.001	Formic acid
				<i>Para</i>	Grey ^b	300	2.174	1.025	Chloroform
4	55	45	HCl	<i>Ortho</i>	Orange ^a	318	2.365	1.75	<i>m</i> -cresol
				<i>Meta</i>	Brick red ^a	320	—	1.051	Nitrobenzene
				<i>Para</i>	Dirty yellow ^b	320	0.978	1.015	Chloroform
5	65	35	HCl	<i>Ortho</i>	Orange ^a	315	2.325	1.92	<i>m</i> -cresol
				<i>Meta</i>	Brick red ^a	320	0.687	1.042	Nitrobenzene
				<i>Para</i>	Orange ^b	320	0.861	1.002	Chloroform
6	75	25	HCl	<i>Ortho</i>	Red ^a	320	2.307	1.83	<i>m</i> -cresol
				<i>Meta</i>	Pink ^a	320	0.683	1.072	Nitrobenzene
				<i>Para</i>	Orange ^b	320	0.668	1.015	Chloroform
7	50	50	H ₂ SO ₄	<i>Ortho</i>	Orange ^a	340	1.817	—	<i>m</i> -cresol
				<i>Meta</i>	Orange ^a	333	1.14	1.08	Nitrobenzene
				<i>Para</i>	Cream ^b	320	0.536	1.018	Chloroform
8	50	50	3% NaOH	<i>Ortho</i>	Dark yellow ^a	300	1.856	—	<i>m</i> -cresol
				<i>Meta</i>	Dirty yellow ^a	310	0.617	1.05	Formic acid
				<i>Para</i>	Grey ^a	320	0.534	1.101	<i>m</i> -cresol
9	50	50	5% NaOH	<i>Ortho</i>	Dark yellow ^a	300	1.842	—	<i>m</i> -cresol
				<i>Meta</i>	Dirty yellow ^a	310	0.615	1.02	Formic acid
				<i>Para</i>	Grey ^a	320	0.532	1.115	<i>m</i> -cresol
10	50	50	7% NaOH	<i>Ortho</i>	Dark yellow ^a	300	1.821	—	<i>m</i> -cresol
				<i>Meta</i>	Dirty yellow ^a	310	0.620	—	Formic acid
				<i>Para</i>	Grey ^a	320	0.53	1.015	<i>m</i> -cresol

^a Amorphous.^b Crystalline.

shown in Figure 1 for the condensate OHAP-PCBA-F, also verified from IR spectra.



The above structure of the repeat unit is indicated by characteristic IR bands (Fig. 2). The presence of a strong band at 1430 cm⁻¹ for C—H bending and at ~ 3000 cm⁻¹ for C—H stretching vibrations of the methylene bridge illustrates the polymeric nature. The band at 3700 cm⁻¹ is characteristic of the phenolic —OH group confirming hydrogen bonding. Carboxylate anion stretching is observed

as a broad band in the region of ~ 1660. The two bands near 690 and 770 cm⁻¹ are caused by C—Cl stretching. The C—H bending vibration of the —CH₃ group is present at 1490 cm⁻¹. The bands near 750 and 830 cm⁻¹ are characteristic of the *p*- and *m*-substituted benzene moiety, respectively.

The prepared resins were found to be highly soluble in a wide range of polar solvents in the moderate or strongly hydrogen-bonded category. However, with the solvents of weak hydrogen-bonding capability, the resins from chlorobenzoic acids were almost unswellable.

Thermal Analysis

The TG thermograms of nine typical resins are presented here (Fig. 3) to give a comparative picture. The characteristic thermal data including glass-

Table II Properties of Resins with Chloro Benzoic Acid as Comonomer

Sl. No.	Molar Ratio of Monomers		Catalyst	Substituted Chlorobenzoic Acid	Colour/Structure	Decomposition Temperature (°C)	Density (gm/cm ³)	Inherent Viscosity (dL/gm)	Solubility
	OHAP : CBA								
1	2	3	4	5	6	7	8	9	
1	25	75	HCl	<i>Ortho</i>	Pink ^b	225	0.112	1.08	DMSO
				<i>Para</i>	White ^a	270	1.032	1.020	Dioxan
2	35	65	HCl	<i>Ortho</i>	Light brown ^b	225	0.354	1.009	DMSO
				<i>Para</i>	White ^a	270	1.336	1.021	Dioxan
3	45	55	HCl	<i>Ortho</i>	Light brown ^b	225	0.584	1.015	DMSO
				<i>Para</i>	Glossy cream ^a	270	1.225	1.020	DMF
4	55	45	HCl	<i>Ortho</i>	Light brown ^b	225	1.2	1.031	DMSO
				<i>Para</i>	Cream ^a	270	0.359	1.020	DMF
5	65	35	HCl	<i>Ortho</i>	Light brown ^b	225	0.349	1.096	DMSO
				<i>Para</i>	White ^a	270	0.489	1.018	DMF
6	75	25	HCl	<i>Ortho</i>	Deep orange ^b	225	1.112	0.010	Ethylacetate
				<i>Para</i>	White ^a	270	0.851	1.018	DMF
7	50	50	H ₂ SO ₄	<i>Ortho</i>	Yellow ^b	225	0.118	1.12	Ethylacetate
				<i>Para</i>	Orange ^b	270	1.244	1.020	DMF
8	50	50	3% NaOH	<i>Ortho</i>	Pink ^a	220	0.252	1.031	Ethylacetate
				<i>Para</i>	Pink ^a	270	0.967	1.015	<i>m</i> -cresol
9	50	50	5% NaOH	<i>Ortho</i>	Pink ^a	220	0.25	1.028	Ethylacetate
				<i>Para</i>	Pink ^a	270	0.957	1.015	<i>m</i> -cresol
10	50	50	7% NaOH	<i>Ortho</i>	Pink ^a	220	0.12	1.025	Ethylacetate
				<i>Para</i>	Pink ^a	270	0.971	1.015	<i>m</i> -cresol

^a Amorphous.

^b Crystalline.

transition temperature, T_g , oxygen index, OI, and integral procedure decomposition temperature, IPDT, are presented in Table III along with the weight-loss pattern and decomposition ranges.

Values calculated here are based on the weight of the carbonaceous char related by the empirical equation

$$0.1 \times 100 = 17.5 + 0.4 \times CR. \quad (1)$$

The thermal stability is evaluated by Doyle's method⁹ involving calculation of the IPDT, that is, determined by summing up the whole shape of the normalized data curve because it is consistently available from the curvilinear data record of the

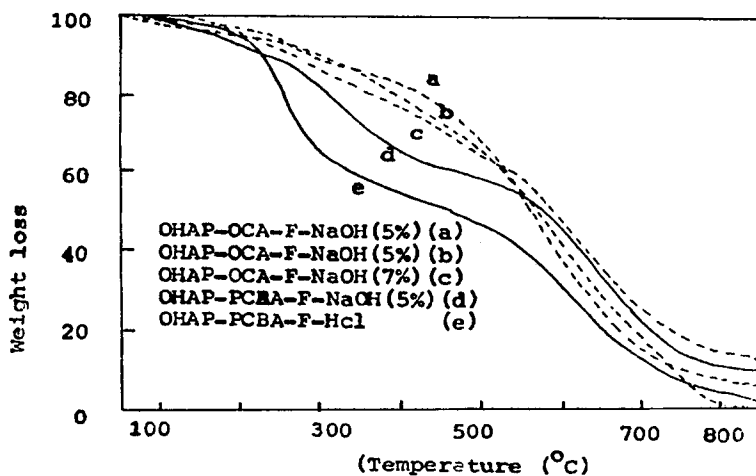


Figure 1 Plausible copolymer structure for the condensate OHAP-PCBA-F.

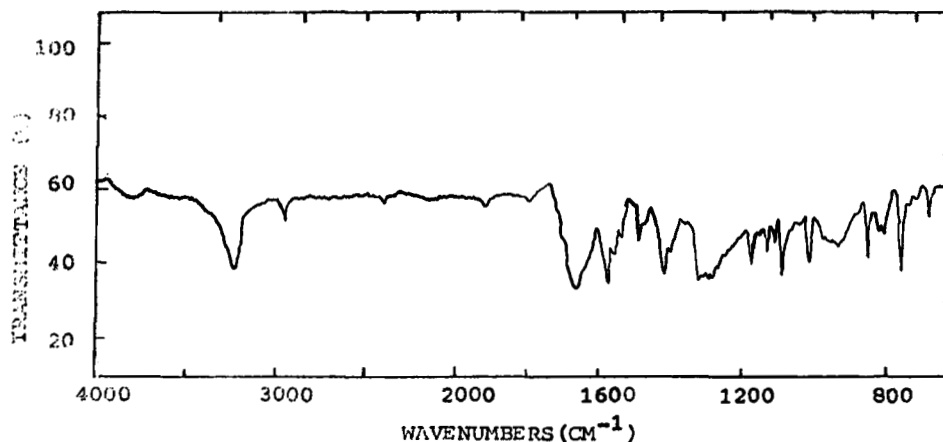


Figure 2 IR spectrum of *o*-hydroxy acetophenone-*p*-chlorobenzoic acid-formaldehyde resin.

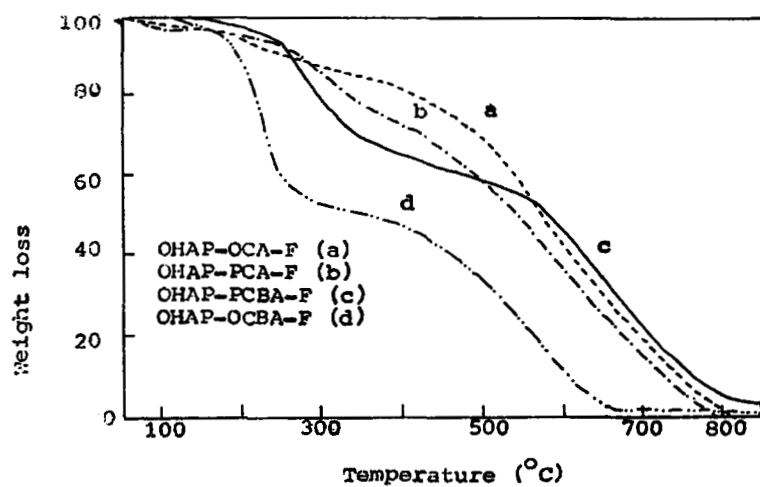


Figure 3(a) TG thermogram of the resins: a, (---), OHAP-OCA-F-H₂SO₄; b, (- - - -), OHAP-PCA-F-H₂SO₄; c, (—), OHAP-PCBA-F-H₂SO₄; d, (- · · · · ·), OHAP-OCBA-F-H₂SO₄.

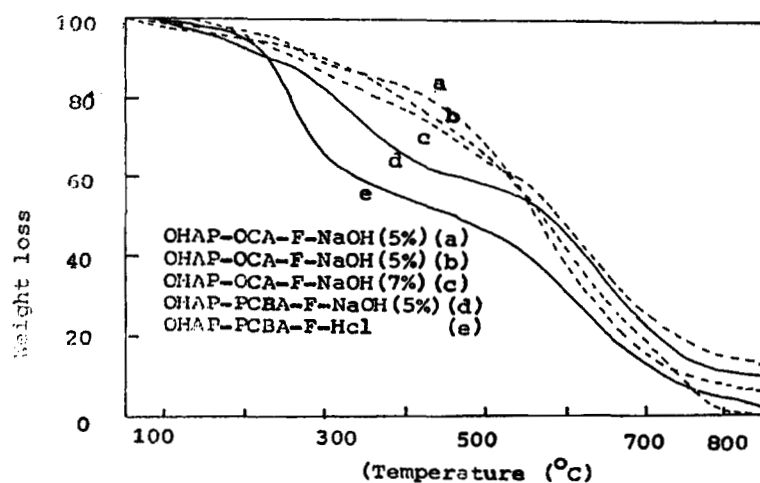


Figure 3(b) TG thermogram of the resins: a, (---), OHAP-OCA-F, NaOH (5%); b, (- - -), OHAP-OCA-F, NaOH (5%); c, (- · · · · ·), OHAP-OCA-F, NaOH (7%); d, (—), OHAP-PCBA-F, NaOH (5%); e, (—), OHAP-PCBA-F-HCl.

Table III Characteristic Thermal Data

Sl. No.	Resin ^a	Catalyst	Weight Loss ($\pm 2\%$)			Decomposition Ranges				T_g	IPDT
			200°C	400°C	600°C	First ^b	Second ^c	Third ^d	O.I. ^e		
1	OHAP-OCA-F	H ₂ SO ₄	3.95	18.42	60.00	50–120	120–290	290–650	—	184.13	331.65
2	OHAP-OCA-F	NaOH (3%)	5.21	23.41	51.49	50–130	130–350	350–770	0.223	184.37	352.28
3	OHAP-OCA-F	NaOH (5%)	7.13	20.86	58.37	50–150	150–270	290–690	0.199	241.00	327.19
4	OHAP-OCA-F	NaOH (7%)	4.32	22.55	60.72	—	50–260	260–800	0.175	263.70	332.70
5	OHAP-PCA-F	H ₂ SO ₄	4.20	27.53	66.50	50–140	140–340	340–700	—	248.61	310.11
6	OHAP-OCBA-F	H ₂ SO ₄	10.40	50.11	90.80	50–120	120–420	420–670	0.183	168.92	148.64
7	OHAP-PCBA-F	H ₂ SO ₄	1.31	20.70	53.80	50–130	130–430	430–810	0.191	251.44	237.35
8	OHAP-PCBA-F	HCl	6.74	46.53	65.31	50–150	150–430	430–810	0.184	195.37	213.50
9	OHAP-PCBA-F	NaOH (5%)	5.40	34.37	55.12	50–130	130–420	420–810	0.216	257.14	296.17

^a Analyzed at a heating rate of 20°C/min in air.

^b Weight loss caused by retained moisture.

^c Major decomposition stage.

^d Secondary decomposition.

^e $0.1 \times 100 = 17.5 + 0.4CR$.

thermogram by the relation

$$IPDT = (T_B - T_A)A^*K^* + T_A \quad (2)$$

where T_A , temperature where volatilization starts; T_B , final test temperature; A^* , total area under the curve; K^* , ratio of the doubly crosshatched area and the rectangular area bounded by T_A^* and T_B ($T_A^* = (T_B - T_A)A^* + T_A$).

Kinetic parameters have been evaluated by the Freeman-Anderson¹⁰ and Broido¹¹ methods. These provide the overall kinetic parameters averaged out for the experimental temperature range, but possess the added disadvantage that the observations at the extreme end are erratic and inexplicable. Here for calculations sake, the complete thermogram is divided into three distinct sigmoids because the resins under observation will not break down in a simple manner. For the individual sigmoid taking the residual weight of the pyrolyzed product at the beginning of that sigmoid to be 100%, the change in structure at each and every instant of pyrolysis affects the rate of decomposition and mechanism.

Though the two cited methods involve a laboriously lengthy method for evaluation of kinetic data, they are attempted because of their merit in using a single thermogram. The Freeman-Anderson method¹⁰ makes use of eq. (3), where a plot of $\Delta \log(-dw/dt)$ and $\Delta \log \bar{w}$ values (evaluated at a constant $\Delta 1/T$) gives the order of reaction n' as slope and the energy of activation E^* as intercept

$$\Delta \log(-dw/dt) = n \Delta \log \bar{w} - (E^*/2.303R)(\Delta 1/T) \quad (3)$$

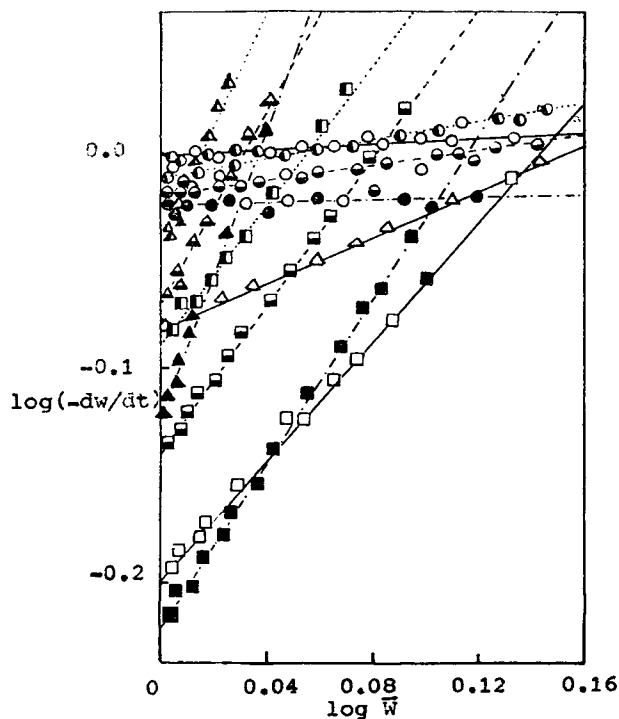


Figure 4 Typical Freeman-Anderson¹⁰ plot for the determination of activation energy (E^*) and order of reaction (n) for the system

	States of decomposition		
	1st	2nd	3rd
a, (—) OHAP-OCA-F-H ₂ SO ₄	○	□	△
b, (---) OHAP-PCA-F-H ₂ SO ₄	●	■	▲
c, (····) OHAP-PCBA-F-H ₂ SO ₄	◐	◑	◒
d, (-·-·-) OHAP-OCBA-F-H ₂ SO ₄	◓	◔	◕

According to the Broido method,¹¹

$$\begin{aligned} \text{for } n = 1 \quad \log \ln(I/Y) \\ &= (E^*/2.303R)(1/T) + K \\ n = 2 \quad \log(I/Y - 1) \\ &= -(E^*/2.303R)(1/T) + K \quad (4) \end{aligned}$$

where K , any constant; Y , normalized weight (w_t/w_0); E^* , energy of activation obtained from the slope of the most appropriate plot.

Freeman-Anderson¹⁰ and Broido¹¹ plots for some selected acid (H_2SO_4) catalyzed resins, OHAP-OCA-F, OHAP-PCA-F, OHAP-PCBA-F, and OHAP-OCBA-F are displayed in Figures 4 and 5, respectively and the kinetic parameter data are tabulated in Table IV.

A cursory glance at Table III shows that all the resins under study decompose in three distinct steps. The initial slow weight loss up to temperatures of 140–150°C is attributed to moisture retained in the sample. The resins from chloro anilines exhibit a slow weight loss in their second decomposition stage up to a temperature of 300°C for a depletion of 20% of their initial weight, followed by a gradual weight loss in the final stage. But the resins from chlorobenzoic acids display a major weight loss of about 40% in the temperature range ~ 130 –420°C. The change in catalyst has a small affect in the observed weight-loss pattern.

On the basis of the observed trend in weight loss with temperature, the plausible degradation mechanism may be outlined with the knowledge that the degradation with phenolic and carboxylic resins occur in three distinct steps,^{12,13} chain-fragmentation and postcuring controlled by unreacted methylol group; thermal reforming, controlled by free radicals formed; ring stripping, depending upon elemental composition, and, also that the normal mode of degradation is thermooxidative.¹⁴

The greater degree of weight loss with chlorobenzoic acids can be attributed to an easier decarboxylation and ring fission, but with chloro anilines the $-\text{NH}_2$ group at the initial step are converted to the $-\text{NO}_2$ group allowing only a small weight loss.

For the resin OHAP-OCA-F (No. 1, Table III), the initial 4% weight loss up to 120°C can be attributed to the retained moisture. In the temperature range of 120–290°C, this degrades to 18.4%, which can be accounted for by the removal of Cl_2 and CO_2 by decarboxylation (the first step being the oxidation of $-\text{COCH}_3$ group to $-\text{COOH}$ group) and oxidation of $-\text{NH}_2$ group. This is in good agreement with the theoretical weight loss of another 16.9%. The consecutive gradual weight loss up to 60% at 600°C, makes one conclude that along with the cleavage of the methylene bridge, which amounts to only 10%, the benzene ring is decomposed to smaller fragments.

Similarly for OHAP-OCBA-F (No. 6, Table III), the major decomposition in the temperature range

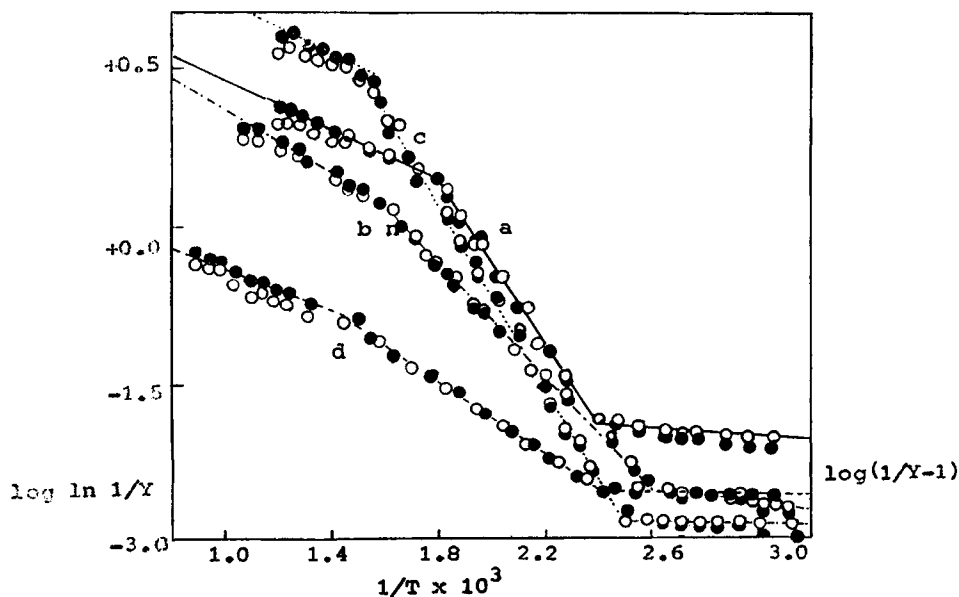


Figure 5 Typical Broido¹¹ plot for the determination of activation energy (E^*). Plots: (○) $\log \ln 1/Y$ vs. $1/T \times 10^3$; (●) $\log(1/Y - 1)$ vs. $1/T \times 10^3$; for the system: (a) (—) OHAP-OCA-F- H_2SO_4 ; (b) (---) OHAP-PCA-F- H_2SO_4 ; (c) (···) OHAP-PCBA-F- H_2SO_4 ; (d) (-·-) OHAP-OCBA-F- H_2SO_4 .

Table IV Kinetic Parameters for Decomposition Ranges

Resin	Energy of Activation (kcal/mol)						Order		
	First		Second		Third		First	Second	Third
	A	B	A	B	A	B	A	A	A
OHAP-OCA-F	0.76	0.29	17.90	18.10	7.62	7.50	0.069	1.50	0.50
OHAP-PCA-F	1.60	1.83	12.90	11.90	6.80	6.40	0.170	1.80	2.27
OHAP-OCBA-F	0.83	0.91	8.18	10.40	4.20	4.60	0.34	1.70	2.20
OHAP-PCBA-F	2.10	2.70	20.30	20.10	7.30	8.20	0.03	2.28	3.10

A, Broido method.¹¹

B, Freeman-Anderson method.¹⁰

120–420°C can be explained by taking into consideration the decarboxylation, which theoretically accounts for 48.7% and matches well with the observed 50.1% weight loss.

Perusal of Table III shows that the resins possess high T_g values in some cases as high as 263.7°C for OHAP-OCA-F-NaOH (7%), the lowest value being 184.1°C for OHAP-OCA-F-H₂SO₄. It was observed that with parachlorobenzoic acids and anilines the T_g value was comparatively greater than the *ortho*-substituted ones. Further alkali-catalyzed resins showed higher T_g values, the value increasing with concentration of alkali.

Though specific analytical procedures were not followed, based on the mass of carbonaceous char, it can be concluded that the resins are not good flame retardants, as evidenced by low oxygen index. However, the alkali-catalyzed ones are less flammable. On the whole the resins under study possess greater thermal stability as evidenced by IPDT values.

From the typical Freeman-Anderson¹⁰ plot, it is evident that a considerable number of experimental points are crowded near the zero abscissa value. Similarly the Broido method¹¹ allows approximation for $n = 1$ and 2 only. Therefore a perfect straight-line plot is never obtained, which requires a plot of equations corresponding to an infinite set of n values to reach an exact E^* value. By making this assumption and as seen from the Freeman-Anderson's calculations,¹⁰ the order lies in the range 1–2 for the major decomposition step (second stage of decomposition). The energy of activation values are in good agreement taking into consideration an error of $\pm 0.1\%$ for the mode of calculation. However, the indicated values of order of reactions are less sensitive because considerable ranges are averaged with little relation to weight change and a detailed kinetic treatment.

In summary, the kinetic parameters obtained with the two different modes are in good agreement with each other. Splitting the thermogram into three distinct sigmoids gives permissible deviations in the value of E^* calculated by both methods.

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