# Synthetic Resins. VI. Studies on Reactivity Ratios, Thermal Behavior, and Bacteriocidal Properties of Resins Prepared from Substituted Acetophenones

SANTOSINI PATRA, ANIL PRASAD DAS, SUBASINI LENKA, and PADMA L. NAYAK, *Laboratory of Polymers and Fibers, Department of Chemistry, Ravenshaw College, Cuttack 753003, Orissa, India*

## Synopsis

The reactivity ratios, thermal behavior, and the bacteriocidal properties of the resins prepared from substituted acetophenones, i.e., *m*-aminoacetophenone, *o*-hydroxyacetophenone, and *m*-hydroxyacetophenone, have been investigated. The results obtained from the bacteriocidal studies are found to be quite interesting. Some of the resins synthesized are potent bacteriocides. The simple Kelen–Tüdös linear graphical method was used to determine the order of reactivity of substituted acetophenones when they are copolymerized with halogen-substituted anilines, i.e., *o*-chloroaniline, *m*-chloroaniline, and *p*-chloroaniline. The resins are found to be thermally stable and the energy of activation have been evaluated from TG curve by applying the Freeman–Anderson and Broido methods.

## INTRODUCTION

The synthesis of several hydroxy, amino and other substituted benzoic acid–formaldehyde resins have been reported along with their use as fungicides, bacteriocides, and ion-exchangers and also their thermal stability meeting the demand of the space age.[1-8] In our program of studying the pharmacological activity of synthetic resins, we have reported[9] that some selective resins are found to highly sensitive to bacteria like *Salmonella typhosa* para B, *Staphylococcus aureus*, and *Pseudomonas pyocyanus*. Considering the reactivity ratio, it has been reported that the composition of a copolymer normally depends on the relative reactivity of the monomeric species. The reactivity ratios $r_1$ and $r_2$ have been determined by various procedures such as linear,[10] nonlinear,[11] computer programming routines,[12] etc. In the present investigation Kelen–Tüdös linear graphical method[13,14] has been used to determine the reactivity ratio $r_1$ and $r_2$. Thermal stability of the resins prepared have also been investigated.

## EXPERIMENTAL

The resins were prepared according to the procedure described in our previous communications.[9,15]

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### Antibacterial Activity

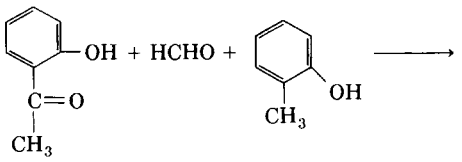
The bacteriocidal properties of the resins numbering 1–7 were studied against the following bacteria: (a) *Staphylococcus aureus*, (b) *Staphylococcus citrus*, (c) *Bacillus subtilis*, (d) *Escherichia coli*, (e) *Klebsiella*, and (f) *Pseudomonas pyocyanus*.

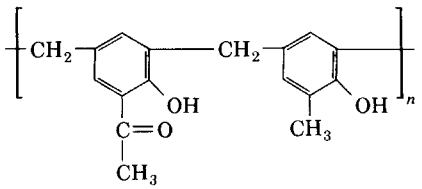
### Thermal Behavior

Thermal analyses were recorded with a thermal analyzer-781 series (Stanton Redcroft, U.K.) in nitrogen at a heating rate of 20°C/min.

## RESULTS AND DISCUSSION

The polycondensation reaction may be represented as follows:





The structure of the repeat unit is confirmed by the IR spectra. The resin shows the characteristic IR bands (Fig. 1) near 2900 $cm^{-1}$ for C—H stretching and near 1480 $cm^{-1}$ for C—H bending vibrations of methylene groups present in the polymer chain. The band near 3440 $cm^{-1}$ is characteristic of the phenolic OH group confirming the hydrogen bonding in *o*-hydroxyacetophenone. The bands at 1660 and 1380 $cm^{-1}$ are due to $-\overset{\overset{O}{\|}}{C}-$ and C—H bending vibrations of the $-CH_3$ group.

### Reactivity Ratios

The reactivity ratios $r_1$ (halogen-substituted anilines) and $r_2$ [comonomer *m*-aminoacetophenone (MAAP) or *m*-hydroxyacetophenone (MHAP) or *o*-hydroxyacetophenone (OHAP)] were calculated from the composition of the copolymers (1–9) and their corresponding monomer feed by using the following equation developed by Kelen and Tüdös (KT),

$$\frac{x(y-1)}{(\alpha y + x^2)} = \left(r_1 + \frac{r_2}{\alpha}\right)\frac{x^2}{\alpha y + x^2} - \frac{r_2}{\alpha} \tag{1}$$

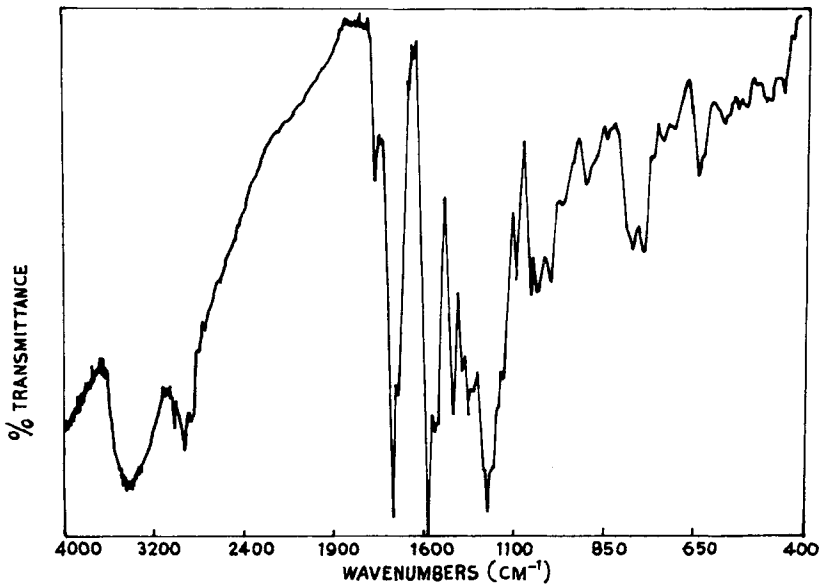



Fig. 1. IR spectrum of *o*-hydroxyacetophenone–*o*-cresol–formaldehyde.

where $x$ is the ratio of mole fractions of monomer 1 ($M_1$) and monomer 2 ($M_2$) in the feed, $y$ is the ratio of mole fractions of $M_1$ and $M_2$ in the copolymer, $\alpha$ is a constant and is given by

$$\alpha = \frac{x_{\min} \cdot x_{\max}}{(y_{\min} \cdot y_{\max})^{0.5}}$$

Equation (1) can be expressed in the form of a linear relationship between $\eta$ and $\xi$, where

$$\eta = \frac{x(y-1)}{\alpha y + x^2}$$

$$\xi = \frac{x^2}{\alpha y + x^2}$$

Equation (1) becomes

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \tag{2}$$

Hence from the plot of $\eta$ vs. $\xi$, the values of $r_1$ and $r_2$ can be calculated (Fig. 2). It has been observed from the plots that the experimental points are reasonably in good agreement with eq. (2). The values of $r_1$ and $r_2$ computed from the plots are presented in Table I.

The reciprocal of the reactivity ratio $r$ expresses the relative strength of different monomers when they are copolymerized with a given comonomer. When MAAP or MHAP (as comonomers) are copolymerized with *o*-chloraniline (OClA), *m*-chloroaniline (MClA), and *p*-chloroaniline (PClA), the reciprocal of the reactivity ($1/r_1$) has the following order:

$$m\text{-ClA} > p\text{-ClA} > o\text{-ClA}$$

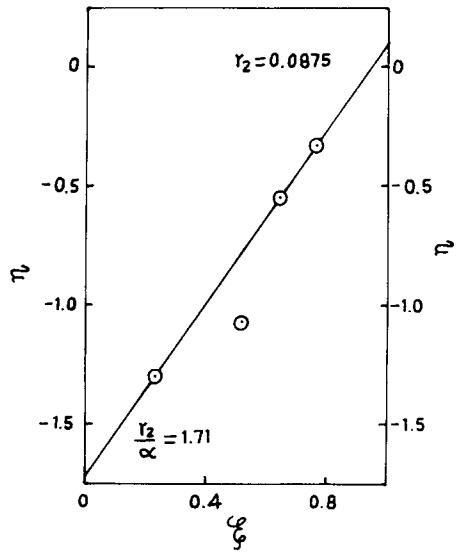



Fig. 2. Kelen–Tüdös plot for the copolymerization system of *m*-hydroxyacetophenone and *o*-chloroaniline.

This is in agreement with the base strength of the amines. However, when these halogen–substituted anilines are copolymerized with OHAP, their reactivity ($1/r_1$) follows the order:

$$o\text{-ClA} > p\text{-ClA} > m\text{-ClA}$$

i.e., in the reverse order of their basic strength.

This reversal of the sequence of reactivity of halogen–substituted anilines may be interpreted on the basis of two important factors: (1) polarization of the comonomers (MAAP, MHAP, or OHAP) as a result of electron attracting

TABLE I
Reactivity Ratios for Copolymerization System (1–9)[a]

| No. | Comonomer | $r_1$ | $r_2$ |
|---|---|---|---|
| Common monomer: *m*-aminoacetophenone ($M_2$) | | | |
| Copolymer 1 | *o*-Chloroaniline ($M_1$) | 0.4425 | 0.3182 |
| Copolymer 2 | *m*-Chloroaniline ($M_1$) | 0.0125 | 0.6315 |
| Copolymer 3 | *p*-Chloroaniline ($M_1$) | 0.015 | 0.8337 |
| Common monomer: *o*-Hydroxyacetophenone ($M_2$) | | | |
| Copolymer 1 | *o*-Chloroaniline ($M_1$) | 0.11 | 0.2801 |
| Copolymer 2 | *m*-Chloroaniline ($M_1$) | 0.155 | 0.6945 |
| Copolymer 3 | *p*-Chloroaniline ($M_1$) | 0.135 | 0.3279 |
| Common monomer: *m*-Hydroxyacetophenone ($M_2$) | | | |
| Copolymer 1 | *o*-Chloroaniline ($M_1$) | 0.1 | 2.2053 |
| Copolymer 2 | *m*-Chloroaniline ($M_1$) | 0.0875 | 0.6454 |
| Copolymer 3 | *p*-Chloroaniline ($M_1$) | 0.095 | 1.3457 |

[a] Calculations are based on the Kelen–Tüdös equation.

or electron donating nature of its substituents, (2) the relative degree of resonance stabilization of the comonomer MAAP which possesses an electron donating ($-NH_2$) as well as an electron attracting ($-\overset{\overset{O}{\|}}{C}-CH_3$) groups. Since the electrophilic group is present at the meta position, it cannot interact with the $-NH_2$ group. Hence it is expected that both these comonomers (MAAP and MHAP) are very weakly polarized. On the other hand, in the case of OHAP, the —OH group can interact with the $-CO-CH_3-$ group causing the molecule to be highly polarized. In the case of *o*-ClA, *m*-ClA, and *p*-ClA, one would expect on the basis of electronegativity of these halogen substituents that the degree of polarization will have the following order: *o*-ClA > *p*-ClA > *m*-ClA. The rate of addition of *o*-ClA with the comonomer OHAP is thus expected to be higher compared to the rate of addition of *p*-ClA or *m*-ClA with OHAP. However, with any weakly polarized comonomers such as MAAP or MHAP, the reactivity of halogen substituted amines is in the same order as their basic strength.

## Antibacterial Activity

Table II represents the sensitivity pattern of seven resins studied against six organisms 30% (w/v) concentration, respectively. The perusal of the results reveals that both the polymers *m*-hydroxyacetophenone–hydroquinone–formaldehyde and *o*-hydroxyacetophenone–acetylsalicylic acid–formaldehyde are found to be highly sensitive against *Bacillus subtillis* and *Pseudomonas pyocyanus* at 30% (w/v) concentration. The polymer *o*-hydroxyacetophenone–acetyl salicylic acid–formaldehyde is moderately sensitive against *Staphylococcus aureus* and *Staphylococcus citrus*, whereas other resins are resistant to the bacteria. But at lower concentration range only the resins *m*-hydroxyacetophenone–hydroquinone–formaldehyde, and *o*-hydroxyacetophenone–acetyl salicylic acid–formaldehyde are found to be moderately sensitive to *Bacillus subtilis* and *Pseudomonas pyocyanus*, but resistant to other bacteria.

The antibacterial action of the resins may be explained by one or more of the following mechanisms:

(i) Injurious effects on cell walls and cell division.
(ii) Effect on the permeability of the cell membrane.
(iii) Effect on enzyme system of the cell.
(iv) Chelation and precipitation of chemicals.
(v) Antimetabolism:
  (a) Oxygen and nitrogen atoms present in the resins can act as hydrogen acceptors in metabolic system and, in doing so, disturb the normal hydrogenation and dehydrogenation reactions in the cell.
  (b) The reactive free radical formed by metabolic breakdown form stable cross linkages with protein and other cellular components.

There is an ambitious program in this laboratory to reveal the antibacteriocidal properties of the resins. More details regarding the antibacteriocidal properties will be discussed in our future communications.

TABLE II
Sensitivity Pattern of Seven Resins at 30% (w/v) Concentration Against Six Organisms[a]

| Sample no. | Name of the resin | Bacteria | | | | | |
|---|---|---|---|---|---|---|---|
| | | *Staphylococcus aureus* | *Staphylococcus citrus* | *Klebsiella* | *Bacillus subtilis* | *Escherichia coli* | *Pseudomonas pyocyanus* |
| 1 | *m*-Hydroxyacetophenone–formaldehyde resin | R | R | R | R | R | R |
| 2 | *m*-Hydroxyacetophenone–formaldehyde resin | R | R | R | HS | R | HS |
| 3 | *m*-Aminoacetophenone–catechol–formaldehyde resin | R | R | R | R | R | R |
| 4 | *m*-Aminoacetophenone–resorcinol–formaldehyde resin | R | R | R | R | R | R |
| 5 | *o*-Hydroxyacetophenone–*o*-cresol–formaldehyde resin | R | R | R | R | R | R |
| 6 | *o*-Hydroxyacetophenone–acetyl salicylic acid–formaldehyde resin | MS | MS | R | HS | R | HS |
| 7 | *o*-Hydroxyacetophenone–sulfanilic acid–formaldehyde resin | R | R | R | R | R | R |

[a] R = resistant; MS = moderately sensitive; HS = highly sensitive.

## Thermal Behavior

Thermogravimetric analysis (TGA) of resins, *o*-hydroxyacetophenone–acetylsalicylic acid–formaldehyde (a) and *m*-hydroxyacetophenone–formaldehyde (b) are shown in Figure 3. The degradation of the resins follow a complex process in which initial weight loss of about 5% is attributed to the loss of moisture retained in the samples, and it is seen that maximum weight loss occurs at 575 and 535°C for the samples (a) and (b) respectively. In order to understand the mechanism of decomposition, the kinetic parameters have been evaluated using the methods of Freeman–Anderson[16] and Broido.[17] The Freeman–Anderson method involves the evaluation of the quantities $\Delta \log(-dw/dt)$ and $\Delta \log \overline{W}$ corresponding to a constant different in $1/T$. According to the equation,

$$\Delta \log\left(-\frac{dw}{dt}\right) = n\Delta \log \overline{W} - \frac{E^*}{2.303R}\Delta\left(\frac{1}{T}\right) \tag{3}$$

The slope of the plot of $\Delta \log(-dw/dt)$ vs. $\Delta \log \overline{W}$ gives order of reaction, $n$, and the intercept on the ordinate gives energy of activation, $E^*$. Figure 4 represents a plot of $-dw/dt$ and $w$ against $1/T$ for the sample b. $dw/dt$ represents the change in weight loss for every 2 min. From this plot the change in weight loss per 0.05 of $1/T$ has been read and after tabulating at the required values $\Delta \log(-dw/dt)$ is plotted against $\Delta \log \overline{W}$ (Fig. 5). The values of $n$ and $E^*$ are found to be 1.5 and 4.00 kcal/mol, respectively.

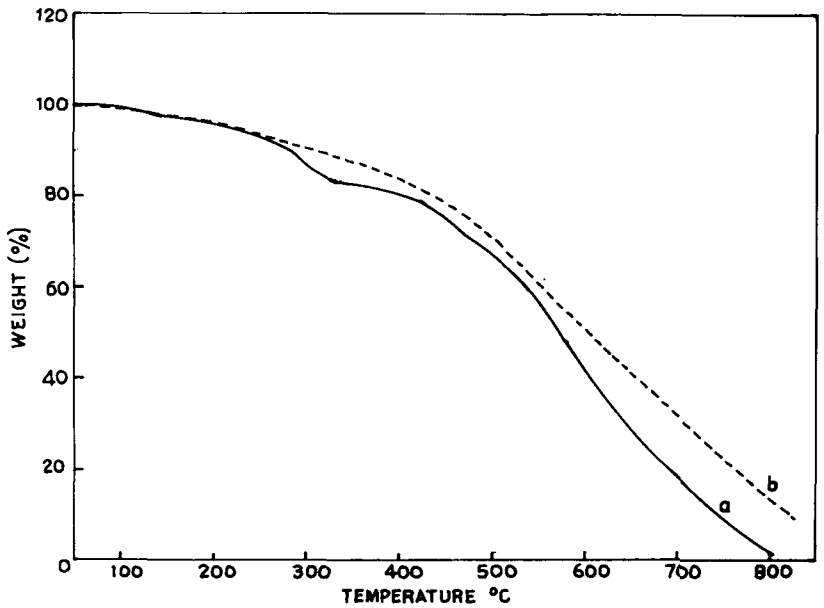



Fig. 3. TGA of *o*-hydroxyacetophenone–acetyl salicylic acid–formaldehyde (a) and *m*-hydroxyacetophenone–formaldehyde (b) resins.

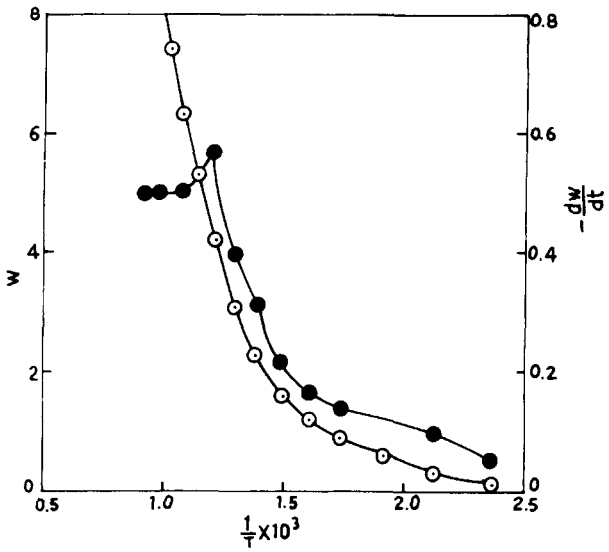



Fig. 4. Plot of $-dw/dt$ and of $w$ against $1/T$ for the resin $m$-hydroxyacetophenone–formaldehyde.

According to the Broido method,

$$\text{for } n = 1,\ \log\ln\left(\frac{1}{y}\right) = -\frac{E^*}{2.303R}\left(\frac{1}{T}\right) + \text{const} \tag{4}$$

$$\text{for } n = 2,\ \log\left(\frac{1-y}{y}\right) = -\frac{E^*}{2.303R}\left(\frac{1}{T}\right) + \text{const} \tag{5}$$

where, $y = W_t/W_0$ being termed as the normalized weight, $W_t$ and $W_0$ are the weights of the material not decomposed at time $t$ and initial weight of the material, respectively. Figure 6 represents a plot of $\log\ln(1/y)$ and $\log[(1 -$

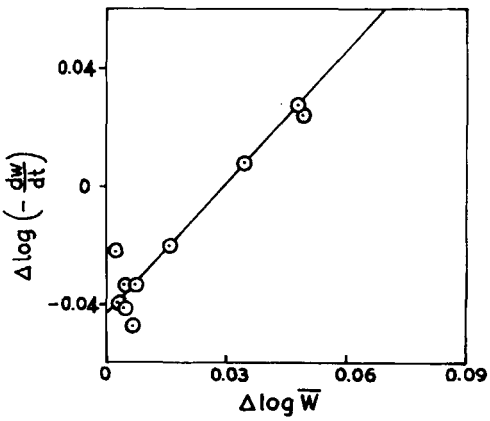



Fig. 5. Freeman–Anderson plot for the determination of activation energy ($E^*$) and order of reaction ($n$) for the resin $m$-hydroxyacetophenone–formaldehyde.

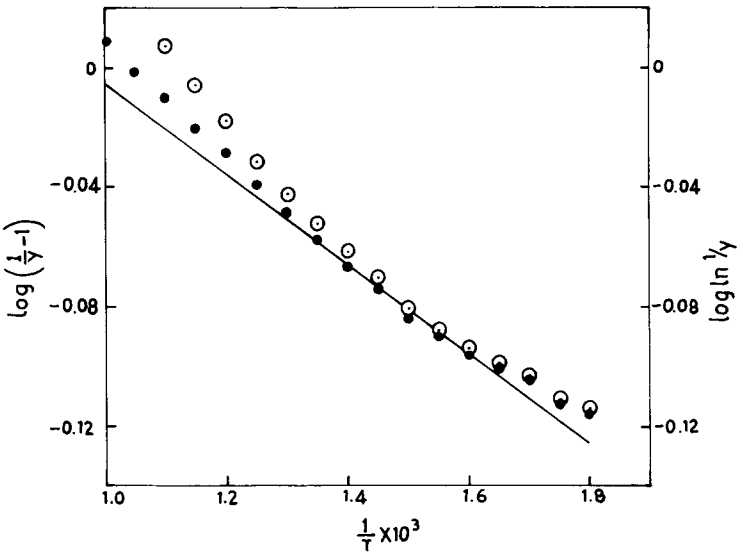



Fig. 6. Typical Broido plot for determination of the activation energy $E^*$ for the resin *m*-hydroxyacetophenone–formaldehyde.

$y)/y]$ vs. $1/T$ for $n = 1$ and $n = 2$, respectively. The slope of the plot gives the value of activation energy to be 4.20 kcal/mol.

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