

Kinetics of the Formation of Dibenzyl Ether Linkage During Curing of Resole-Type Phenol-Formaldehyde Resin by DTA and Infrared Spectroscopy

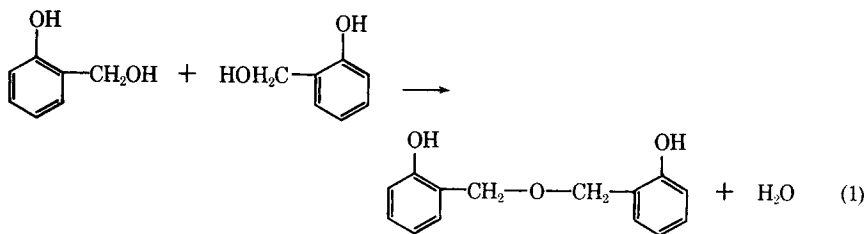
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Synopsis

The kinetics of formation of dibenzyl ether linkages during cure of resole-type phenol-formaldehyde resins was studied by the use of differential thermal analysis and infrared spectroscopy. The activation energy was 21.6 kcal./mole by the Borchard and Daniels method and 18.6 kcal./mole by the Kissinger method. For the same process, infrared spectroscopy gives 19.7 kcal./mole, which shows a rather good agreement between the two different methods. The heat of reaction, determined from the area under the DTA curve for the corresponding reaction, was found to be 20.2 cal./g.

Introduction

In the previous paper¹ the possibility of using DTA and infrared spectroscopic techniques in following the curing of resole-type phenol-formaldehyde resins was pointed out. It was shown that in neutral media the most important reaction is the formation of dibenzyl ether linkages according to the eq. (1).



The present paper reports the kinetic data for the above reaction as obtained from DTA and infrared spectroscopic studies. The evaluation of the kinetics in the case of differential thermal analysis has been made by the methods described by Kissinger² and Borchard and Daniels,³ while for the infrared spectroscopy measurements Gugenheim's method was applied in the same way as done by Conley and Bieron.⁴

Experimental

For the DTA measurements a Gebrüder Netzsch instrument, Type 404, was used with a modified metal block (Fig. 1). The weight of the

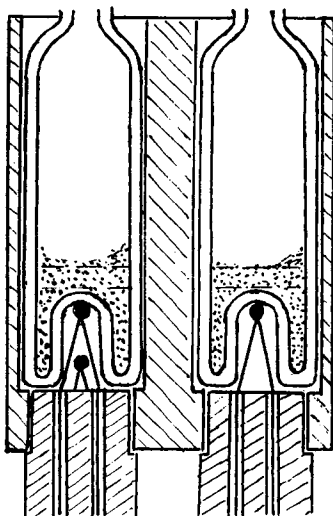


Fig. 1. Metal block with glass tubes used in DTA apparatus.

resin samples and of calcined alumina used as a reference substance was approximately 100 mg. Infrared spectroscopic measurements were conducted on a Perkin-Elmer instrument, Model 221. The resin was dissolved in acetone and cast on a polished NaCl plate. Saligenin was prepared by the method described in the literature,⁵ while the resin was condensed in the same way as described in the previous paper¹ for a phenol/formaldehyde (P/F) ratio of 1:1.5 and with 0.03 mole NaOH per mole of phenol.

Results and Discussion

Sprung⁶ found that the thermal reaction of saligenin without catalyst is second-order with an activation energy of 20.0 kcal./mole. If we use Kissinger's method² for the evaluation of kinetic parameters, we obtain from the shape index of the curve (Fig. 2) a value for the reaction order of 1.9, which is quite satisfactory considering the precision with which the tangents are drawn. From the data shown in Table I an activation energy

TABLE I
Data Obtained by the Use of Kissinger's Method for the Evaluation of Kinetic Parameters for the Thermal Reaction of Saligenin

| Heating rate, ϕ , °C./min. | Temperature at the peak, T_m , °K | $\log (\phi/T_m^2)$ | $(1/T) \times 10^3$, °K. ⁻¹ |
|---------------------------------|-------------------------------------|---------------------|---|
| 2 | 455 | -5.015 | 2.20 |
| 5 | 469 | -4.693 | 2.12 |
| 10 | 489 | -4.378 | 2.04 |
| 20 | 511 | -4.116 | 1.96 |
| 33 | 524 | -3.916 | 1.90 |

for the thermal hardening of saligenin can be estimated by means of eq. (2)

$$d(\ln \phi / T_m^2) / d(1/T) = -E/R \quad (2)$$

by plotting $\ln \phi / T_m^2$ versus $1/T$, where ϕ is heating rate and the other symbols have their usual meaning. A straight line is obtained (Fig. 3), and its slope, multiplied by $2.3R$, gives an activation energy of 17.3 kcal./

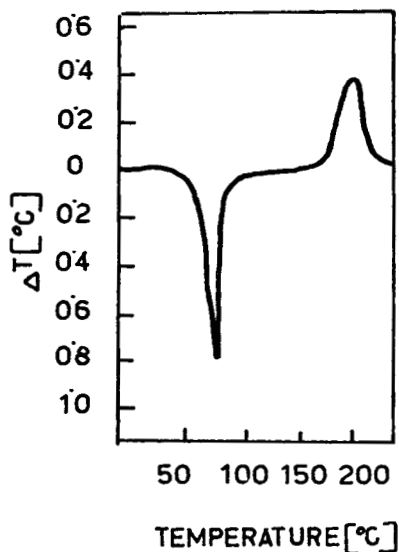


Fig. 2. Thermogram of saligenin. Heating rate 5°C./min.

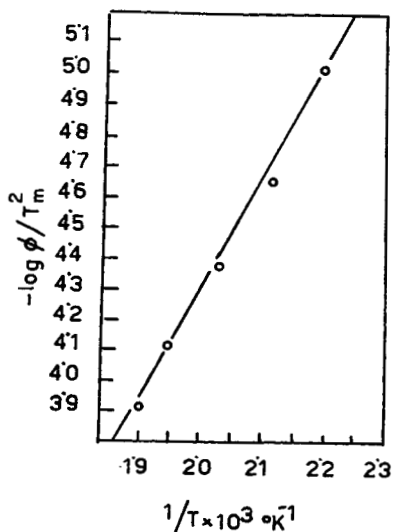


Fig. 3. Changes of ϕ / T_m^2 vs. $1/T_m$ for thermal hardening of saligenin.

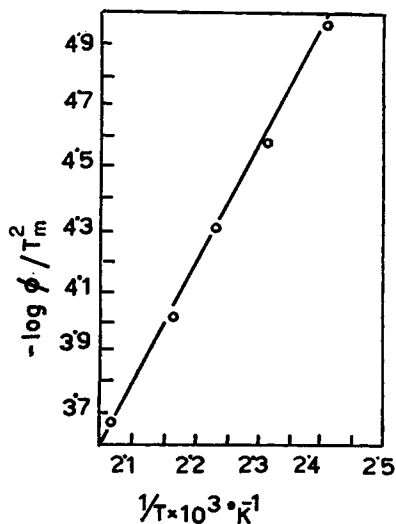


Fig. 4. Plot of $\log \phi / T_m^2$ vs. $1/T_m$ for the formation of dibenzyl ether linkages during the thermal hardening of the resin.

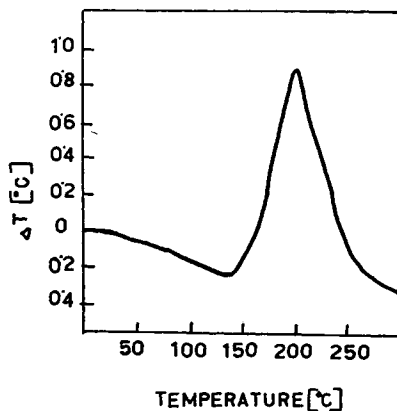


Fig. 5. DTA of the phenolic resin with P/F = 1:1.5 without the peak corresponding to the formation of methylene linkages. Heating rate 50°C./min.

mole. If the same method is applied to the phenol-formaldehyde resin (i.e., to the exothermic peak corresponding to the formation of dibenzyl ether bridges),¹ the shape index shows that this reaction is first order. The activation energy, calculated in the same manner as for saligenin, is 18.5 kcal./mole (Fig. 4). As the reaction of thermal hardening of the resin is first order, it is possible to use the method of Borchard and Daniels² for the evaluation of kinetic parameters. This method was successfully applied for solid inorganic systems;⁷⁻⁹ for decompositions of oxalate and bicarbonate very good agreement was achieved in comparison with classical

methods. Reaction velocity constants can be obtained by this method through eq. (3),

$$k = T/(A - a) \quad (3)$$

where k represents specific reaction rate, T is the height of the DTA curve at the temperature where the measurements are made, A is the area under the DTA curve for a given reaction, and a is the area under the DTA curve preceding the temperature, T .

The thermogram of the resin which was used to compute T , A , and a is shown in Figure 5, while the values obtained from this curve are presented in Table II.

TABLE II

Data Obtained by the Method of Borchard and Daniels from the DTA Thermogram (Fig. 5) for the Evaluation of Kinetic Parameters for the Formation of Dibenzyl Ether Linkages During Resin Cure

| Temp., t , °C. | T , mm. | A , mm. ² | a , mm. ² | $1/T \times 10^3$, °K. | k , sec. ⁻¹ $\times 10^{-2}$ | $\log k$ |
|------------------------|--------------|---------------------------|---------------------------|----------------------------|---|----------|
| 172 | 27.0 | 1696 | 121 | 2.22 | 1.7 | -1.766 |
| 188 | 47.0 | | 318 | 2.17 | 3.4 | -1.467 |
| 203 | 78.0 | | 696 | 2.10 | 7.8 | -1.108 |
| 210 | 83.0 | | 940 | 2.07 | 11.0 | -0.959 |
| 218 | 68.5 | | 1320 | 2.04 | 18.5 | -0.733 |
| 222 | 32.5 | | 1560 | 2.02 | 25.0 | -0.622 |

From the above data an Arrhenius plot (Fig. 6) was constructed according to

$$k = Ae^{-E/RT} \quad (4)$$

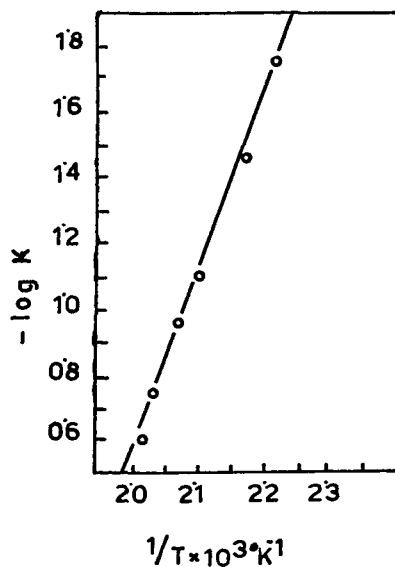


Fig. 6. Arrhenius plot for the formation of dibenzyl ether linkage constructed from the data presented in Table II.

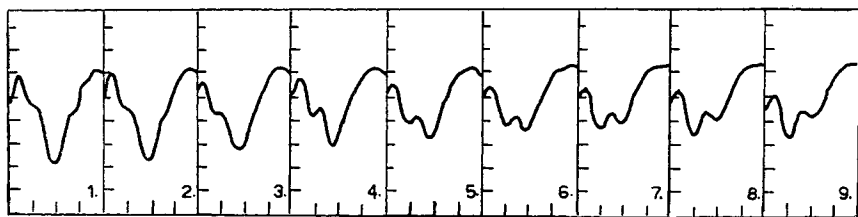


Fig. 7. Changes in the infrared spectrum in the range $950\text{--}1050\text{ cm.}^{-1}$ of the phenolic resin during curing at 110°C. : (1) initial spectrum (0 min.); (2) 30 min.; (3) 60 min.; (4) 90 min.; (5) 120 min.; (6) 150 min.; (7) 180 min.; (8) 210 min.; (9) 240 min.

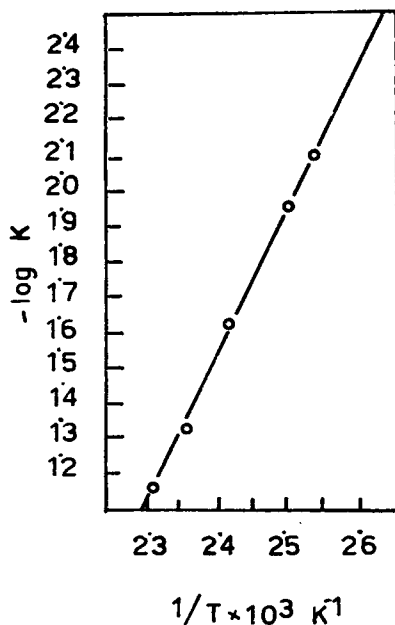


Fig. 8. Change in rate constant vs. absolute temperature for the reaction to ether formation as followed by infrared spectroscopy.

giving an activation energy of $21.6\text{ kcal./mole.}^*$ For the kinetic study of the same reaction by infrared spectroscopic technique, Gugenheim's method was applied in the same way as it was by Conley and Bieron⁵ in their study of oxidative degradation of phenolic resin. The changes in the infrared spectrum during the thermal hardening of the resin are shown in Figure 7. From infrared spectra obtained for every 10°C. between 110 and 160°C. the reaction rate constants were estimated. Figure 8 represents the dependence of the reaction rate on absolute temperature. An activation energy of 19.7 kcal./mole obtained from the slope of the straight line is in

* The methods of Borchard and Daniels and Kissinger, and particularly their applicability to such resin samples, do not afford highly precise determinations of activation energy.

very good agreement with the values obtained by the DTA methods. The heat of formation of dibenzyl ether linkages was determined by use of eq. (5):¹⁰

$$H_s = \frac{A_s \cdot m_r}{A_r \cdot m_s} (H)_r \quad (5)$$

Here H_s and H_r represent the heats of reaction for the sample and reference substance, respectively, A_s and A_r represent the respective areas under the DTA curve, and m_s and m_r represent the respective weights of the sample and reference. The calibration of the apparatus was accomplished through comparison of areas under DTA curves for substances with known thermic effects in the temperature range of the resin cure. The results are shown in Table III. The heat of reaction of formation of ether bridges during resin hardening estimated in this way was 20.2 cal./g.

TABLE III
Data for the Calorimetric Determination of DTA Apparatus

| Substance | Melting point, °C. | Heat of fusion, cal./g. | $m_r H_r / A_r$, cal./g. |
|-------------------|-----------------------|----------------------------|------------------------------|
| Benzoic acid | 122 | 33.9 | 0.272 |
| AgNO ₃ | 208 | 17.7 | 0.280 |
| KNO ₃ | 308 | 25.4 | 0.288 |

The results shown in Table III show that differential thermal analysis and infrared spectroscopy are very useful techniques for the investigation of the chemistry and kinetics of the processes that occur during the hardening of phenolic resin and give information which is almost impossible to obtain by classical methods. This suggests that it should also be possible to apply these methods to similar systems.

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Résumé

La cinétique de formation de liens du type éther dibenzyle en cours de durcissement de résines phénol-formaldéhyde de type résol a été étudiée par analyse thermique différentielle et spectroscopie infrarouge. L'énergie d'activation s'élevait à 21.6 et à 18.6 Kcal, suivant qu'on utilisait la méthode de Borchards Daniels, soit celle de Kissinger.

Pour ce même processus, la spectroscopie infra-rouge indique 19.7 Kcal, ce qui est un record satisfaisant pour deux méthodes différentes. La chaleur de réaction, déterminée au départ de la surface en-dessous de la courbe DTA pour la réaction correspondante était égale à 20.2 cal/g.

Zusammenfassung

Die Kinetik der Bildung von Dibenzylätherbrücken bei der Härtung von Phenolformaldehydharzen vom Resoltyp wurde mittels Differentialthermoanalyse und Infrarotspektroskopie untersucht. Nach der Methode von Borchard und Daniels betrug die Aktivierungsenergie 21.6 kcal, nach derjenigen von Kissinger 18.6 kcal. Für den gleichen Prozess liefert die IR-Spektroskopie einen Wert von 19.7 kcal, was eine recht gute Übereinstimmung zwischen den zwei verschiedenen Methoden bedeutet. Die aus der Fläche unter der DTA-Kurve für die entsprechende Reaktion bestimmte Reaktionswärme betrug 20.2 cal/g.

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