Kinetics of Thermal Polymerization of Shellac.
Part II. Effect of Catalysts

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Synopsis

In the present communication the effect of p-toluenesulfonic acid catalyst on thermal polymerization of shellac has been investigated.   The difference in activation energy for uncatalyzed and catalyzed reaction, has been computed to be 7.4 kcal. when $c = 0.1\%$. The activation energy for uncatalyzed reaction, calculated on this basis comes to 12.5 kcal.

INTRODUCTION

According to observations of previous workers[1-4] various chemicals have a marked catalytic effect on the life under heat (LUH) of shellac. They exhibit two reactions: acceleration or retardation.   Hydroxides, ureas and substituted ureas, amines, and certain organic acids (such as oleic, palmitic, and aleuritic) have been reported as efficient retarders. The action of sodium hydroxide is maximum.   It increases the LUH 99-fold.   On the other hand, certain metallic chlorides and sulfates, urea and salts of urea, aliphatic and aromatic acids have been found to shorten the LUH depending on their concentrations.   In the present paper, an attempt has been made to collect all such data and to interpret them in the light of our present knowledge of chemical reactions followed in the process of polymerization as well as to investigate the action of p-toluenesulfonic acid which is a standard catalyst for all thermosetting resins.

EXPERIMENTAL

The LUH (life under heat) of dried and desiccated dewaxed decolorized shellac was determined at 125, 150, and 175°C. in the usual way.[5]   Then the LUH of shellac containing 0.1, 0.2, 0.3, and 0.5% of catalyst (p-toluenesulfonic acid) were also determined.   Much difficulty was encountered in determination of LUH at high concentrations of the catalyst.

RESULTS AND DISCUSSION

The retarding effect of 10% of various reagents on the LUH of shellac at 150°C. is listed in Table I.[2]   The concentrations of metallic chlorides,

ureas and urea salts, and organic acids, which act as accelerators were plotted against r ($r = t_0/t$, where t_0 and t are LUH values without and with catalyst, respectively) on the basis of data available in the literature,[2] and it was found that they exhibit linear relationship except for urea nitrate, for which a proper explanation is still to be sought.

TABLE I

Retarding Effects of Certain Reagents (10%) on LUH of Shellac at 150°C

Reagent	t/t_0
NaOH	99
KOH	44
Na_2CO_3	36
Dimethyl urea	3.0
Aleuritic acid	1.1

The results of p-toluenesulfonic acids are included in Tables II and III. Plots of r (i.e., efficiency) against catalyst concentration C_{cat} for p-toluenesulfonic acid are indicated in Figure 1.

TABLE II

Dependence of r on Catalyst Concentration and Temperature

C_{cat} %	125°C.		150°C.		175°C.	
	LUH, sec.	r	LUH, sec.	r	LUH, sec.	r
0.1	205	24.9	110	15.3	89	10.8
0.2	127	39.8	68	24.7	65	14.7
0.3	87	58.1	40	42.0	40	23.9
0.5	60	84.3	22	76.4	33	29.0

TABLE III

Relationship between r and Temperature

Temp. T_p, °C.	$10^3 \times 1/T_p$	r_c ($c = 0.1\%$)	$\log r_c$	t_0, sec.	$\log t_0$
125	2.50	24.9	1.4	5057	3.70
150	2.36	15.3	1.2	1680	3.20
175	2.24	10.8	1.0	958	2.98

From Figure 1, it is evident that all plots are linear. These lines could be represented by the equation:

$$r = t_0/t = x + mC_{cat}$$

It is evident from Figure 1 that the slope m of the straight line is dependent on the nature of chemical used as well as on the temperature of polymerization.
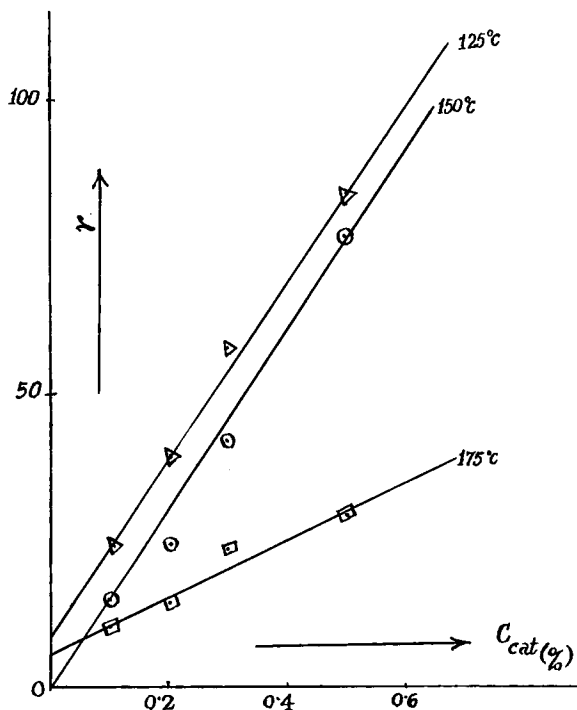
Fig. 1. Dependence of r on the catalyst concentration at different temperatures.

Chemical Behaviors of Catalysts

It would not be out of place to state that the chemical behavior of these catalysts is very difficult to explain as hinted by Gardner,[4] due to certain uncertainties in the process because the reaction can take place between individual lac molecules and also between lac and the added chemical simultaneously.

Previous studies[6] indicate that acetal formation is probably the main reaction of the polymerization process which is catalyzed by hydrogen ion;[7] thus we can ascribe the retarding action of alkalies and other hydroxides to their reaction with the carboxyl group present in shellac. The substituted ureas, amines, and sodium carbonate may retard polymerization in a similar way. The acetates and stearates may retard polymerization by reacting with hydroxyl groups whereas sodium bisulfate, amines, and substituted ureas may also retard polymerization by attacking the aldehyde group present in shellac. However, polyhydroxy acids retard polymerization by introducing a large number of functional groups into the system. The prevention of polymerization of shellac by esterification of hydroxyl groups with saturated fatty acids (acetic, butyric, or caprillic acids) could be explained by the fact that the hydrogen ion of shellac is destroyed by this reaction, which acts as an autocatalyst for the polymerization of shellac.

The accelerating action of catalysts, on the other hand, may be explained on the basis of their specific properties. The accelerating properties of mineral and simple organic acids could be ascribed to their capacities of introducing hydrogen ion into the system. The accelerating properties of certain metallic chlorides, sulfates, and lime could be attributed to their dehydrating properties. The accelerating actions of urea, urea nitrate, and urea oxalate are very difficult to explain, but most probably they enhance the rate of polymerization by adding to the aldehyde content of the system. They may also act as initiators. All these points would be more clear if the polymerization process were known completely.

Dependence of r on Catalyst Concentration and Temperature

From Table II, it is evident that the value of r increases with increase in catalyst concentration and decreases with increase in polymerization temperature, which can be easily explained.

From the previous paper[8] it is apparent that the gelation starts at a definite extent of reaction (say p_c). Let R_{p0} and R_p be rates of polymerization without and with a catalyst at a given temperature and let t_0 and t be the corresponding times taken for the onset of gelation. The equations will be as follows:

$$p_c = R_{p0}t_0$$

$$p_c = R_p t$$

$$t_0/t = R_p/R_{p0} = r$$

Now, it is apparent that with an increase in catalyst concentration R_p would increase and so would the ratio r. Again, we know that for the pre-gelation stage,[8]

$$R_p = K_p$$

Where K_p is the rate constant of polymerization,

Therefore,

$$r_{c,T} = R_{pc,T}/R_{p0,T} = K_{pc,T}/K_{p0,T}$$

or

$$\log r_{c,T} = \log K_{pc,T} - \log K_{p0,T}$$

Again,

$$K_p = Ae^{-E/RT}$$

Thus

$$K_{p0,T} = A_1 e^{-E_1/RT}$$

and

$$K_{pc,T} = A_2 e^{-E_2/RT}$$

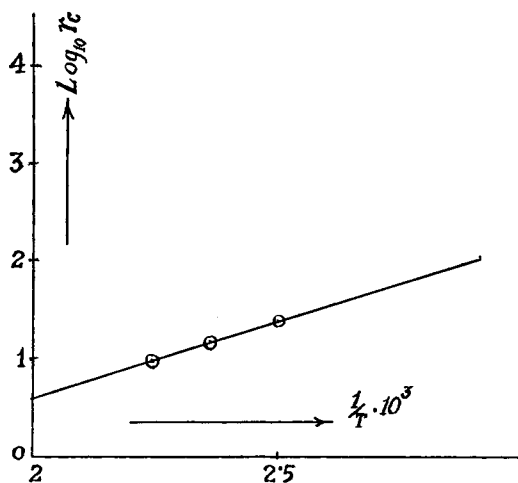$$\log r_{c,T} = \log (A_2/A_1) + [(E_1 - E_2)/2.303RT]$$

Fig. 2. Plot of log r_c vs. the reciprocal temperature ($c = 0.1\%$).

where E_1 and E_2 are the energies of activation of the uncatalyzed and catalyzed reactions, respectively.

It is thus evident that with the increase in polymerization temperature, $\log r_{c,T}$ would decrease, as would the ratio $r_{c,T}$.

The value of $(E_1 - E_2)$ has been found to be 7.4 kcal. from the plot of $\log r_c$ (at $c = 0.1\%$) against $(1/T) \times 10^3$ (Fig. 2), as at higher concentration of catalyst shellac becomes completely brittle and infusible, most probably due to a different kind of polymerization reaction.

Again,

$$p_c = R_{p0}t_0$$

$$R_{p0} = K_{p0}$$

and

$$K_{p0} = A_1 e^{-E_1/RT}$$

Therefore, $\log t_0 = \log p_c - \log A_1 + (E_1/2.303RT)$. So, by plotting $\log t_0$ against $(1/T) \times 10^3$ the value of E_1, the energy of activation for uncatalyzed reaction, was determined to be 12.5 kcal. (Fig. 3).

In addition it is evident from Table II that as the concentration of catalyst increases (i.e., $C_{cat} > 0.1\%$), the fusibility of shellac diminishes, and at higher concentrations of catalyst ($C_{cat} \geq 0.5\%$), the shellac does not melt at all; the whole bulk becomes brittle and infusible due to a different kind of polymerization as indicated above. Moreover, it has been also observed that the fusibility is dependent on the temperature of polymerization. The higher the temperature of polymerization, greater will be fusibility.

Theoretically, the percentage of insolubles present at the gel point at any given temperature of polymerization should be independent of catalyst
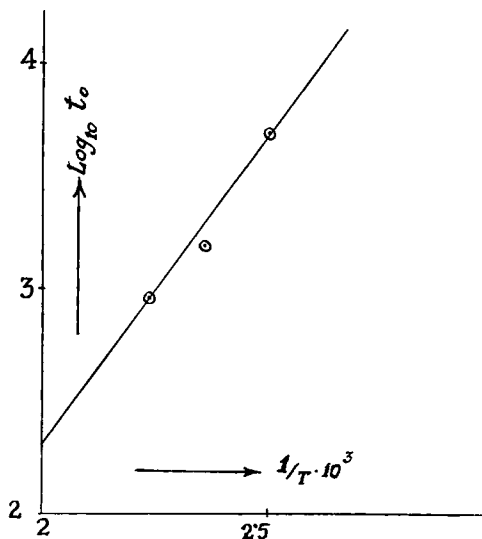
Fig. 3. Plot of log t_0 vs. the reciprocal temperature.

concentration. In the case of shellac, it is very difficult to stop the reaction exactly at the gel point, and at the same time it is also very difficult to make insoluble polymers free of catalysts, as the latter undergoes some type of chemical or physical changes as evidenced by its blackening during polymerization. Therefore, no information in this connection could be obtained

CONCLUSIONS

The accelerating properties of p-toluenesulfonic acid can be ascribed to its hygroscopic nature, since moisture is one of the products of the polymerization reaction. Evidently, it is the most effective accelerating catalyst for heat polymerization of shellac, the efficiency of which is solely dependent on its concentration. Moreover when a given concentration of p-toluenesulfonic acid is reached, the shellac polymerizes instantaneously and becomes infusible and brittle.

References

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Résumé

On étudie dans la présente communication l'effet catalytique de l'acide *p*-toluène sulfonique sur la polymérisation thermique du shellac.   La différence entre l'énergie d'activation de la réaction non-catalysée et la réaction catalysée est évaluée à 7.4 kcal.   Quand $c = 0.1\%$ l'énergie d'activation pour la réaction non-catalysée, calculée sur cette base, devient 12.5 Kcal.

Zusammenfassung

In der vorliegenden Arbeit wurde die katalytische Wirkung von *p*-Toluolsulfonsäure auf die thermische Polymerisation von Schellack untersucht.   Der Unterschied zwischen der Aktivierungsenergie der unkatalysierten und der katalysierten Reaktion wurde zu 7,4 kcal bestimmt.   Für $c = 0,1\%$ ergibt sich für die auf dieser Grundlage berechneten Aktivierungsenergie der unkatalysierten Reaktion der Wert 12,5 kcal.