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## Studies on Aleuritic Acid—Part II: Catalytic Polycondensation

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The kinetics of catalytic polycondensation of aleuritic acid with *p*-toluene sulphonic acid as catalyst has been investigated varying the concentration of catalyst from 0.1 to 1.0 per cent on the weight of aleuritic acid at 140°C., 160°C., 180°C. and 200°C. The catalysed reaction follows the second order of kinetics with respect to the carboxyl concentration, and is much faster than the uncatalysed reaction. While the activation energy of the reaction does not increase appreciably in the catalysed reaction, the frequency factor is nearly 100 times that for the uncatalysed reaction up to 0.3 per cent concentration of the catalyst.

IN the first part of the paper<sup>1</sup> the nature and kinetics of thermal polycondensation were reported. A qualitative result of the catalysed reaction was also reported and a tentative picture of the reaction mechanism proposed. In the present communication the kinetics of catalysed reaction has been studied in detail, varying the concentration of the catalyst and the reaction temperature. The reaction or velocity constant *k*, the energy of activation *E* and the frequency factor *A* have been calculated, and by using the inter-relations between them it has been possible to elucidate the mechanism of the polycondensation.

The velocity constant of the uncatalysed polycondensation of aleuritic acid was calculated from the data reported in the previous paper and compared with the same of the catalysed one. In the present case *p*-toluenesulphonic acid was used as a catalyst in proportions varying from 0.1 to 1.0 per cent on the weight of the aleuritic acid and the reactions were carried out at

temperatures of 140°C., 160°C., 180°C. and 200°C.

### Experimental

5.0 gm. of pure aleuritic acid were dried in a desiccator and then mixed thoroughly with the requisite amount of *p*-toluenesulphonic acid. The mixture was heated in a thin-walled pyrex test-tube, immersed in an oil bath. The bath temperature was maintained within  $\pm 1^\circ\text{C}$ . Dry air was passed continuously through the melt to help stirring as well as to drive out water formed during the reaction. The outlet tube was wrapped up with asbestos tape to prevent the condensation of moisture. Another empty thin-walled test-tube was heated alongside the reaction tube. Pipettes were placed inside this so that these might attain the same temperature at which the reactions were proceeding in the other test-tubes. These pipettes were used to draw samples at different time intervals. Immediately after the samples had been drawn, they were discharged into basins which had been chilled over ice in order to arrest the reaction quickly.

The acid and saponification values of the samples were then determined in the usual way. From these the ester value and the percentage of esterification were calculated, using the relations: Ester value = S.V. - A.V. and percentage of

$$\text{esterification} = \frac{\text{S.V.} - \text{A.V.}}{\text{S.V.}} \times 100.$$

The A.V., S.V. and E.V., as determined at various temperatures at definite time

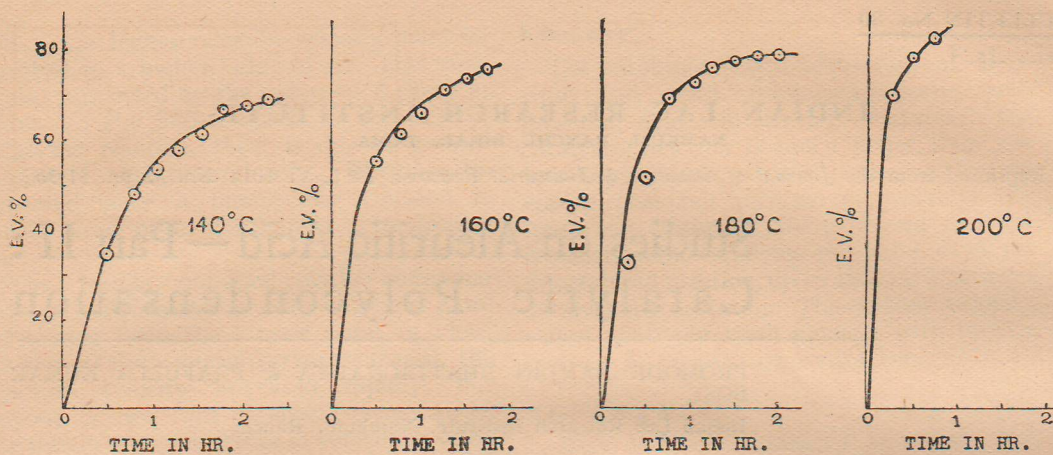


Fig. 1

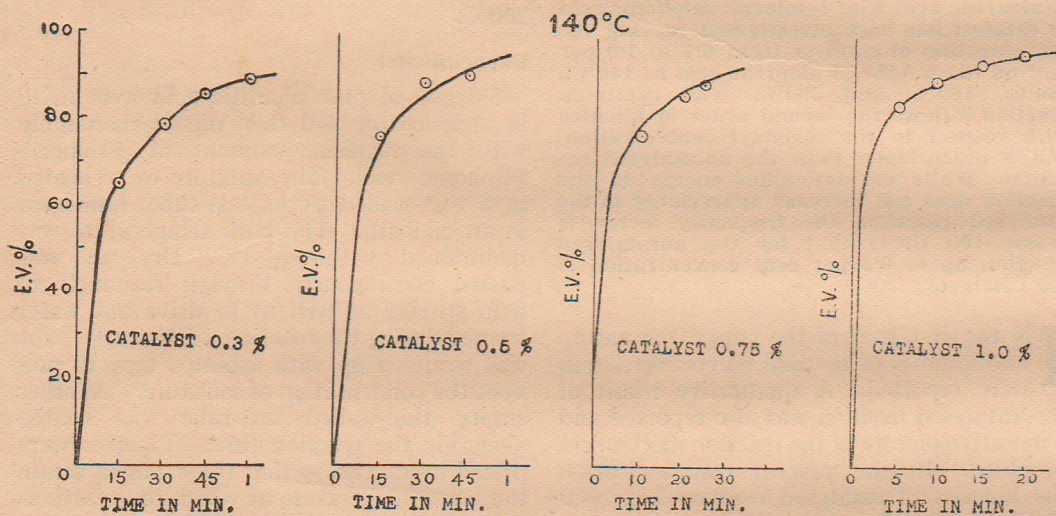


Fig. 2

intervals, are given in Tables I and II, and the corresponding graphs of percentage conversion or esterification against time in Figs. 1 and 2. The activation energy was calculated as described in the previous paper by plotting the log of time to attain 50 per cent conversion against  $\frac{1}{T}$  and noting the slope of the resulting straight line. The data are given in Table III and the graph in Fig. 3. The value of the activation energy was found to be not very different from the value obtained previously in the case of the uncatalysed reaction, namely 15.6 K-cal.

For a more detailed kinetic consideration, the degree of polymerization, i.e.  $\frac{1}{1-p}$  (where  $p$  = the extent of reaction) was calculated from Tables I and II. The corresponding graphs are given in Figs. 4 and 5.

The reaction constant  $k$  for uncatalysed reaction was calculated from the data available in the previous paper from the slope of the curve  $\frac{1}{(1-p)^2} - t$  using the relation  $k = \frac{\text{slope}}{2Co^2}$ . In the present case of catalysed reaction, however, the calculation was made

TABLE I

 (5 gm. of aleuritic acid + 0.1 per cent of *p*-toluenesulphonic acid)

TEMP., °C.	TIME OF REACTION, hr.	A.V.	S.V.	E.V., %	<i>p</i>	$\frac{1}{1-p}$
140	0.50	141.9	215.5	34.0	0.34	1.515
	0.75	112.4	214.7	47.6	0.48	1.923
	1.00	95.59	215.9	53.88	0.54	2.173
	1.25	90.12	215.8	58.25	0.58	2.380
	1.50	83.56	214.7	61.20	0.61	2.564
	1.75	71.61	216.2	67.36	0.67	3.030
	2.0	69.11	216.2	68.03	0.68	3.125
2.25	66.62	215.7	69.13	0.69	3.225	
160	0.25	125.4	215.6	41.82	0.42	1.724
	0.50	96.18	215.2	55.30	0.55	2.22
	0.75	84.74	215.3	61.12	0.61	2.564
	1.0	73.99	215.5	65.66	0.66	2.941
	1.25	61.45	215.9	71.69	0.72	3.571
	1.50	56.18	215.7	73.96	0.74	3.841
	1.75	51.59	214.8	75.98	0.76	4.016
180	0.25	105.2	214.9	33.22	0.33	1.492
	0.50	86.74	214.8	51.69	0.51	2.04
	0.75	66.70	215.2	69.02	0.69	3.225
	1.0	59.17	215.6	72.54	0.72	3.571
	1.25	49.56	215.1	76.95	0.77	4.347
	1.50	46.34	215.3	78.41	0.78	4.545
	1.75	44.29	215.9	79.49	0.79	4.761
2.0	43.46	216.4	79.75	0.80	5.000	
200	0.25	64.45	214.8	70.81	0.70	3.333
	0.50	45.55	215.6	78.84	0.79	4.761
	0.75	35.20	216.2	83.71	0.84	6.250
	1.0					

Polymerized substance insoluble in alcohol, benzene or alcohol-acetone mixture

TABLE II

(Aleuritic acid, 5 gm.; temp., 140°C.)

CATALYST, %	TIME OF REACTION, min.	A.V.	S.V.	E.V., %	<i>p</i>	$\frac{1}{1-p}$
0.3	15	91.66	255.2	64.07	0.64	2.77
	30	54.54	254.8	78.56	0.78	4.54
	45	38.95	254.6	84.72	0.85	6.66
	60	29.09	255.0	88.59	0.89	9.09
	75					
0.5	15	37.71	262.2	75.63	0.75	4.06
	30	33.09	263.1	87.40	0.87	7.69
	45	24.42	261.9	90.67	0.91	11.11
	60					
0.75	10	48.79	206.3	76.35	0.76	4.16
	20	28.59	205.8	86.10	0.86	7.14
	25	24.18	206.9	88.28	0.88	8.333
	35					
	1.0	5	39.74	239.0	83.35	0.83
10		38.02	238.5	89.67	0.89	9.25
15		27.91	238.0	94.58	0.94	16.66
20		23.92	237.3	95.39	0.95	20.00
25						

TABLE III

(Catalyst concentration, 0.1 per cent)

TEMP., °C.	$\frac{1}{T}$	TIME TAKEN TO REACH 50% ESTERIFICATION, min. (t)	log t	ACTIVATION ENERGY (E)
140	0.00242	52	1.7160	12.01 K-cal.
160	0.00232	27	1.4314	
180	0.00222	16	1.2041	
200	0.00212	7	0.8451	

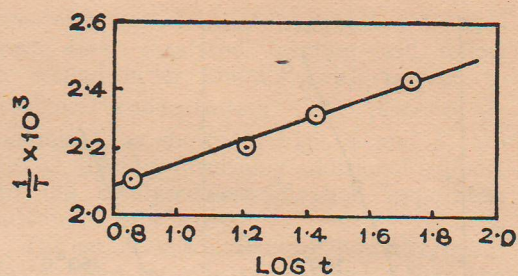


FIG. 3

from the graph of  $\frac{1}{1-p}$  against  $t$ , using the equation  $k = \frac{\text{slope}}{C_0}$ . The data for different temperatures are given in Table IV.

On plotting  $\log k$  against  $\frac{1}{T}$  the value of  $\log A$  is readily obtained, as  $\log A$  is the intercept on the  $\log k$  axis. The values of  $A$  calculated from  $\log A$  are given in Table V. Fig. 6 shows the plot of  $\log k$  against  $\frac{1}{T}$  for both catalysed and uncatalysed reactions.

The time taken to reach 50 per cent conversion with varying catalyst concentrations at 140°C. and other temperatures was obtained from the graph of percentage conversion against time. The data are given

TABLE IV

TEMP., °C.	CATALYST ADDED, %	TIME FOR 50% CONVERSION, min.	<i>k</i>
140	Nil	222	$1.24 \times 10^{-5}$
160	Nil	155	$2.36 \times 10^{-5}$
180	Nil	45	$9.26 \times 10^{-5}$
200	Nil	21	$23.9 \times 10^{-5}$
140	0.1	52	$4.72 \times 10^{-3}$
160	0.1	27	$9.25 \times 10^{-3}$
180	0.1	16	$14.7 \times 10^{-3}$
200	0.1	7	$33.2 \times 10^{-3}$
140	0.3	8	$3.93 \times 10^{-2}$
140	0.5	5	$7.31 \times 10^{-2}$
140	0.75	$3\frac{1}{2}$	$10.5 \times 10^{-2}$
140	1.0	2	$28.0 \times 10^{-2}$

TABLE V

TEMP., °C.	$\frac{1}{T} \times 10^3$	<i>k</i>	log <i>k</i>	<i>A</i> × 10 <sup>4</sup>
<i>Aleuritic acid without catalyst</i>				
140	2.42	$1.24 \times 10^{-5}$	0.0934	2.985
160	2.32	$2.36 \times 10^{-5}$	0.3729	
180	2.22	$9.26 \times 10^{-5}$	0.9666	
200	2.12	$23.9 \times 10^{-5}$	1.37	
<i>Aleuritic acid with 0.1 per cent catalyst</i>				
140	2.42	$4.72 \times 10^{-3}$	0.6739	3.758
160	2.32	$9.25 \times 10^{-3}$	0.9661	
180	2.22	$14.7 \times 10^{-3}$	1.1673	
200	2.12	$33.2 \times 10^{-3}$	1.5211	

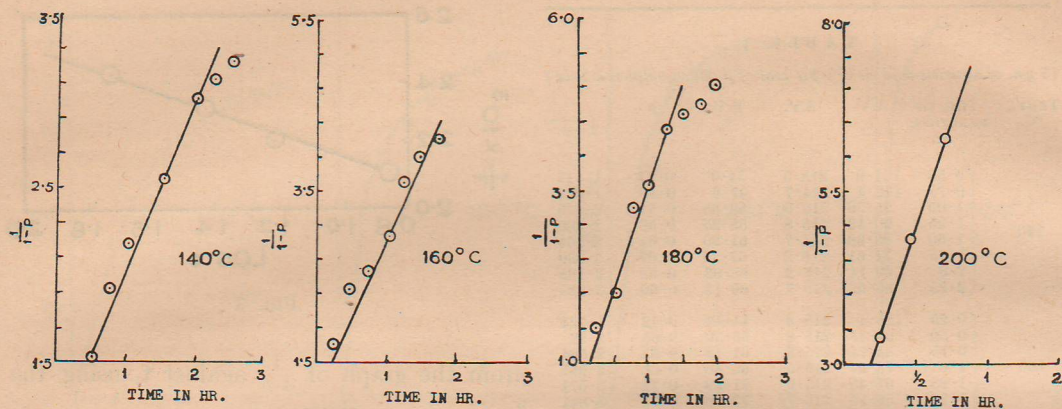


FIG. 4

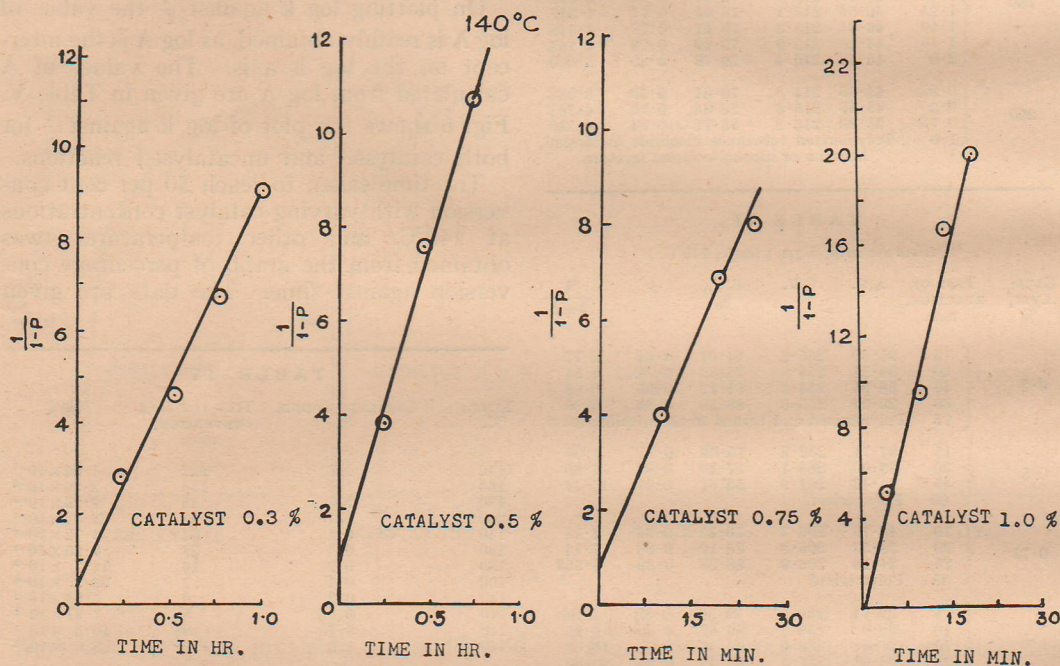


FIG. 5

in Table IV, the corresponding graphs being shown in Figs. 7 and 8.

The time of attaining 50 per cent conversion was plotted against the percentage of catalyst and the graph in Fig. 7 was obtained. It may be noticed that up to a certain point the reaction velocity increases markedly with an increase in the concentration of the catalyst, but beyond this point, the reaction

velocity undergoes comparatively small increase as will be evident from the flat nature of the curve.

#### Discussion

In the previous paper it was shown that uncatalysed auto-condensation of aleuritic acid is a third order reaction, one molecule of the carboxyl acid itself behaving as

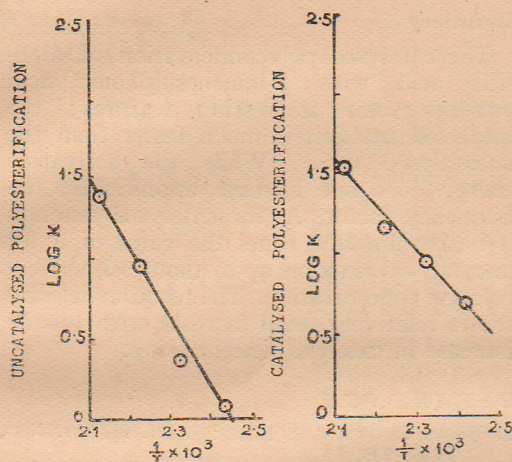


FIG. 6

the catalyst. If that assumption be correct, then catalysed reaction will follow a second order kinetics, with respect to carboxyl concentration. The plots of  $\frac{1}{1-p}$  against  $t$ , as shown in Figs. 4 and 5, are linear, thereby furnishing additional support to the catalysed esterification hypothesis advanced previously.

The catalysed reactions are, however, much faster than the uncatalysed one. Now the

velocity constant  $k$  is equal to  $Ae^{-\frac{E}{RT}}$ , where  $E$  is the activation energy and  $A$ , a frequency factor. Therefore, an increase in the value of  $k$ , the reaction velocity, would mean that  $E$  will be smaller and  $A$  greater for catalysed than for uncatalysed reaction. Table III shows, however, that the activation energy for the catalysed reaction is not very different from that of the uncatalysed one.

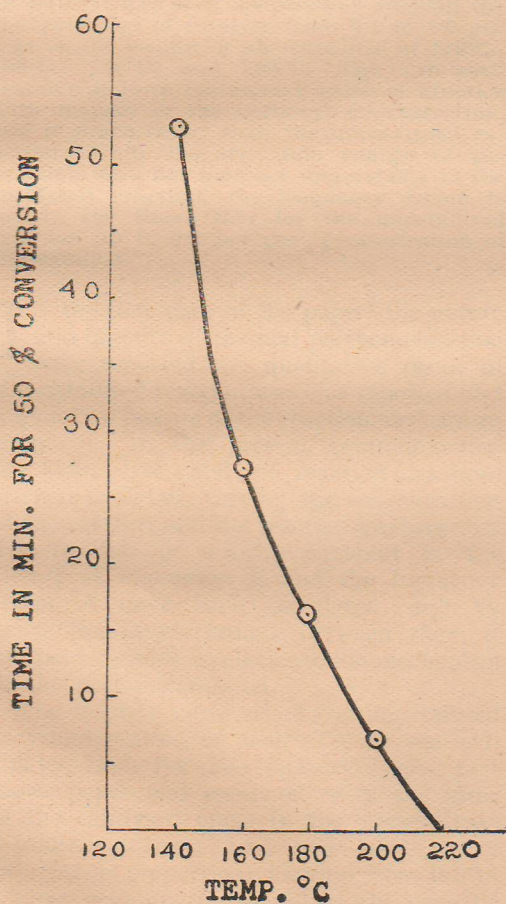


FIG. 7

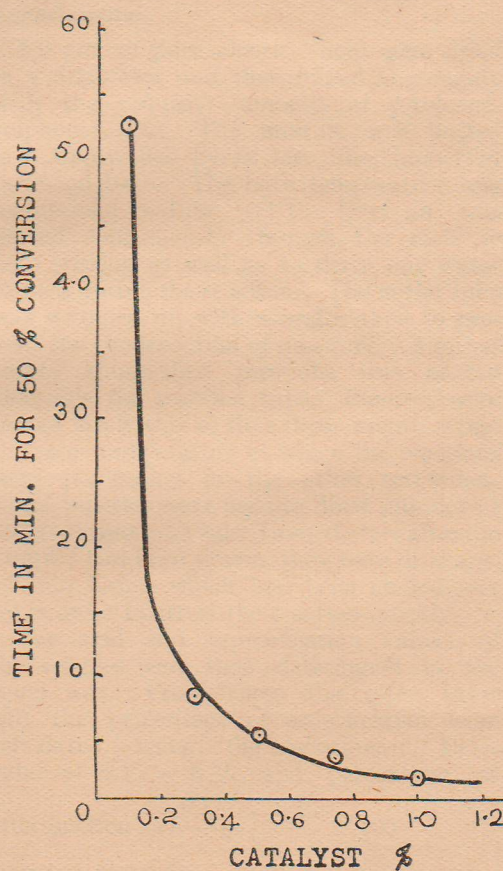


FIG. 8

Hence, the higher reaction velocity must be ascribed to a higher value of  $A$ . This view is also supported by the values of  $A$  given in Table V. The higher speed in the case of catalysed reaction, then, is due to greater number of effective collisions. This may be expected since a bimolecular collision is much more probable than a termolecular one.

The results obtained with increasing catalyst concentration are, however, more interesting from the kinetic point of view. As the catalyst concentration increased, the reaction velocity increased rapidly, but beyond 0.3 per cent catalyst concentration, the proportionate increase in velocity became very slight.

#### Summary

The catalysed polycondensation of aleuritic acid with *p*-toluenesulphonic acid presents some interesting features; the catalysed reaction is much faster than the uncatalysed one. While the activation energy does not increase appreciably, the frequency factor,  $A$ , for catalysed reaction is nearly hundred times the value of  $A$  for uncatalysed reaction, up to about 0.3 per cent catalyst concentration. The reaction velocity shows relatively small increase with further increase in catalyst concentration.

#### REFERENCE

1. BASU, BHOWMIK & BOSE : *J. sci. industr. Res.*, 1948, **7B**, 153.