

# The Kinetics of the Polymerization Reaction of Toluene Diisocyanate with HTPB Prepolymer

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## SYNOPSIS

The uncatalysed and catalysed polymerization of a hydroxyl-terminated polybutadiene with toluene diisocyanate has been studied in toluene solution at four different temperatures. The rate constants ( $k_1$ ,  $k_2$ ) and the activation parameters ( $Ea_1$ ,  $Ea_2$ ,  $\Delta S_1^\ddagger$ ,  $\Delta S_2^\ddagger$ ) for the isocyanate groups in the 4 and 2 positions were calculated. It was found that the catalysts enhance the reactivity of the 2 position isocyanate group rather than the 4 position isocyanate group. It was also found that diethylcyclohexylamine has higher selectivity than dibutyltin dilaurate to enhance the reactivity of the isocyanate group in the 2 position. The effect of solvent has also been studied. The reactivity decreased in the following order; benzene = toluene > chlorobenzene > dioxane > nitrobenzene. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Hydroxyl-terminated polybutadiene (HTPB) is a popular binder<sup>1</sup> used in solid rocket propellants. The polybutadiene chain gives higher energy value and better mechanical properties. Low viscosity of this prepolymer favours high solid loading (fuel and oxidizer). The major problem associated with HTPB is the high reactivity of primary hydroxyl groups with toluene diisocyanate (TDI, curing agent) and hence suffers from lower pot life.<sup>2</sup>

The use of hydroxylated liquid polybutadiene resin in polyurethane synthesis has been observed.<sup>3-5</sup> It is an important raw material for production of polyurethane elastomers. The nonpolar hydrocarbon main chain of HTPB provides superior hydrolytic stability. The polybutadiene-urethanes are having combined properties of polyether and ester urethane systems as well as conventional rubbers.<sup>6</sup>

The kinetics of model urethane formation reaction between isocyanate and alcohols has been extensively studied.<sup>7-12</sup> However, comparatively little information has been reported on the diisocyanate-

diol reaction kinetics.<sup>13-17</sup> The difficulty is mainly due to the increase of viscosity during the polymerization reaction. Yee and Adicof f<sup>18</sup> reported the copolymerization kinetics in propellants of the HTPB-isophoron diisocyanate system. Recently Coutinho and co-workers<sup>19-22</sup> reported the uncatalysed reaction rates of HTPB with different diisocyanates.

The presence, nature, and concentration of the catalyst affects the properties of the polymer.<sup>23</sup> Reaction medium is also one of the important factors in polymer synthesis. The kinetics of the catalysed reaction of HTPB with TDI has not been studied.

The aim of the present work is to study the effect of amine and tin catalysts on the polymerization reaction of HTPB having primary hydroxyl group with TDI having two different reactive groups.

## EXPERIMENTAL

### Materials

HTPB obtained from Vikram Sarabhai Space Centre ( $M_w = 2500$ ; hydroxyl value = 43.6 mgKOH/gm) was used as received. TDI obtained from Fluka containing 80% 2,4-TDI and 20% 2,6-TDI isomers was distilled at reduced pressure and used. Dibutyltin dilaurate (DBTDL; Merck) was used as re-

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ceived. Diethylcyclohexylamine (DECHA; Sigma) was distilled before use. Benzene, chlorobenzene, nitrobenzene, dioxane, and toluene were purified by the reported procedure.<sup>24</sup>

### Polymerization and Rate Measurement

Polymerization for different time intervals were carried out in individual reactors. The reactors were assembled with a 100-mL conical flask containing 5 g of HTPB, 10 mL of toluene, and a silicon rubber tube attached nitrogen inlet-outlet tube. The re-

actors were purged with nitrogen and closed with a silicon rubber cap and were immersed in a constant temperature bath with stirring. A specially fabricated multimagnetic stirrer was employed. After thermal equilibrium was attained, 5 mL of 0.8M TDI toluene solution was injected through the rubber tube. The concentration with respect to the reactant was 0.2M and the —NCO/—OH ratio was unity. After each time interval, the reactor was removed from the bath and 5 mL of 2M dibutylamine solution was added. The flask was kept for 12 h to ensure complete reaction of the unreacted isocyanate with

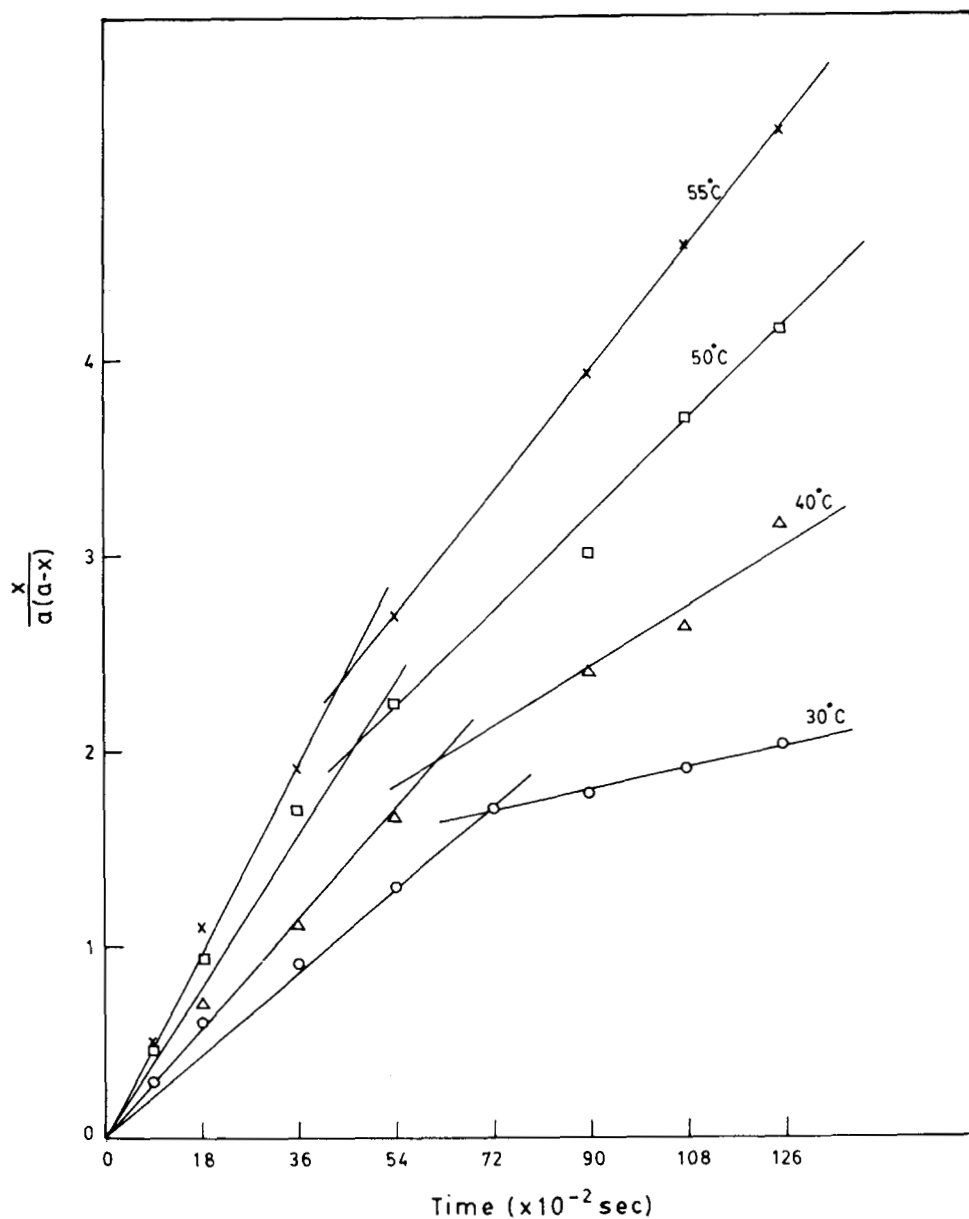


Figure 1 Uncatalysed second-order TDI-HTPB reaction plots.

the amine. The excess amine was measured by titration with 0.48M alcoholic hydrochloric acid. Before titration, 5 mL of toluene and three drops of methyl red methylene blue mixed indicator<sup>25</sup> were added. In the case of catalysed experiments, the calculated amount of catalyst was taken along with the solvent.

## RESULTS AND DISCUSSION

The uncatalysed and catalysed polymerization reactions of HTPB with TDI were carried out at four

different temperatures (30, 40, 50, and 55°C). Representative rate plots are given in Figures 1, 2, and 3. The data were treated according to a second order rate equation for equal initial reactant concentrations. Second order rate plots for both uncatalysed and catalysed reactions show very distinct breaks in continuity beyond the 13% conversion. Coutinho and Rocha<sup>21</sup> observed pronounced discontinuity at 25% conversion in an uncatalysed reaction. Thus, this behaviour may be due to the difference in reactivity of the isocyanate groups in the TDI molecule. The —NCO group in position 4 is not deactivated by the methyl substituent in position 1. Under the

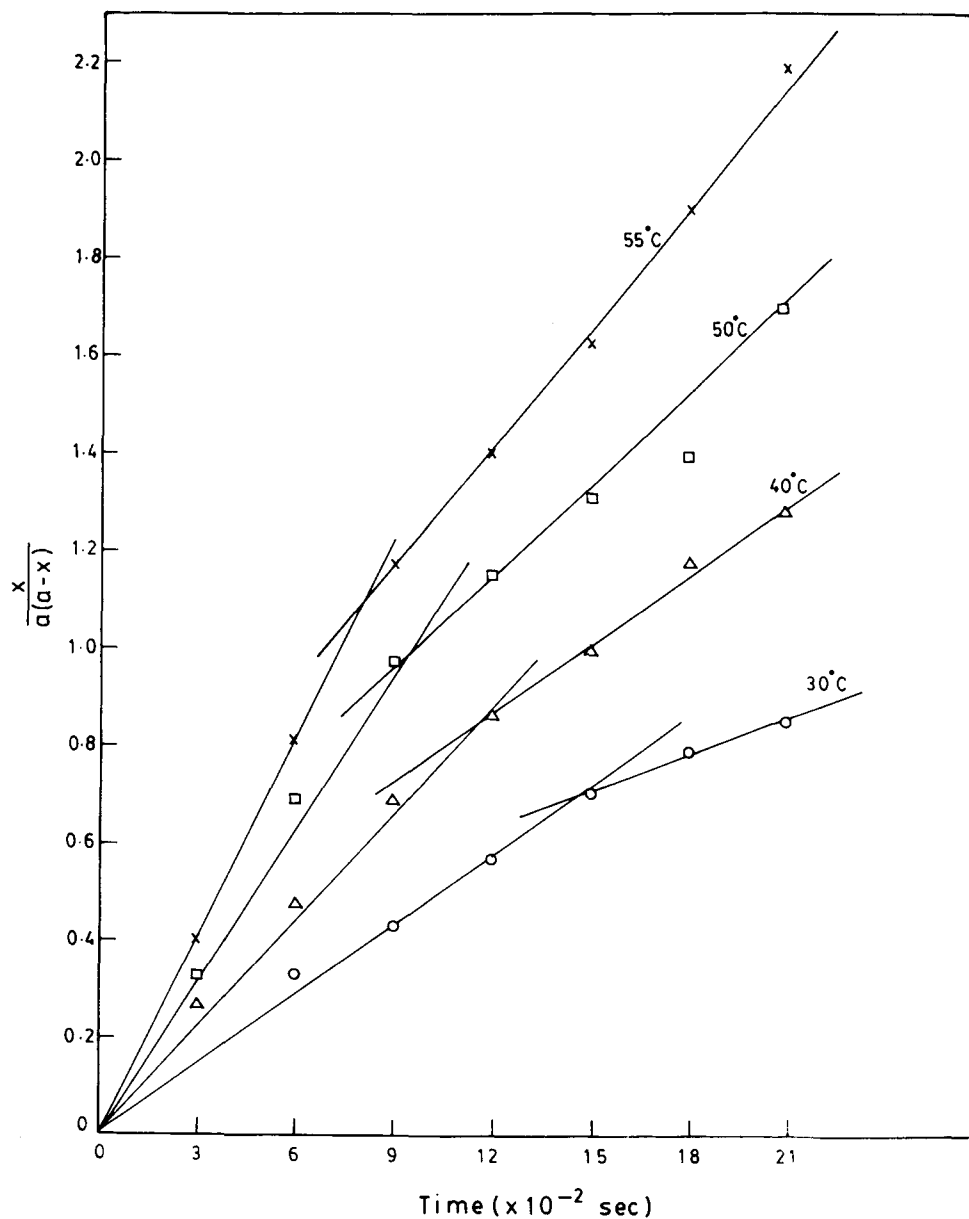


Figure 2 Diethylcyclohexylamine catalysed second-order TDI-HTPB reaction plots.

same time it is also activated by the isocyanate group in position 2. Simultaneously the —NCO group in position 2 is activated by the isocyanate group in position 4 but it is blocked and deactivated by the methyl group in position 1. The isocyanate group in the *para* position is more reactive than the isocyanate group in the *ortho* position.<sup>13</sup> The —NCO group in the *ortho* position may be reacted after consumption of the —NCO group in the 4 position. According to this argument the break point should appear at around 50% conversion, but it is observed

below 15% conversion. Thus it may be concluded that the —NCO group in the 2 position can react simultaneously with the —NCO group in the 4 position after some extent of reaction.<sup>7</sup>

Table I shows the rate constants and activation parameters for the uncatalysed and diethylcyclohexylamine, dibutyltin dilaurate catalysed reactions. Diethylcyclohexylamine has not been used for the urethane polymerization reaction. It is now found that this tertiary amine has appreciable catalytic activity even at a concentration of  $10^{-3}M$ . Thirty

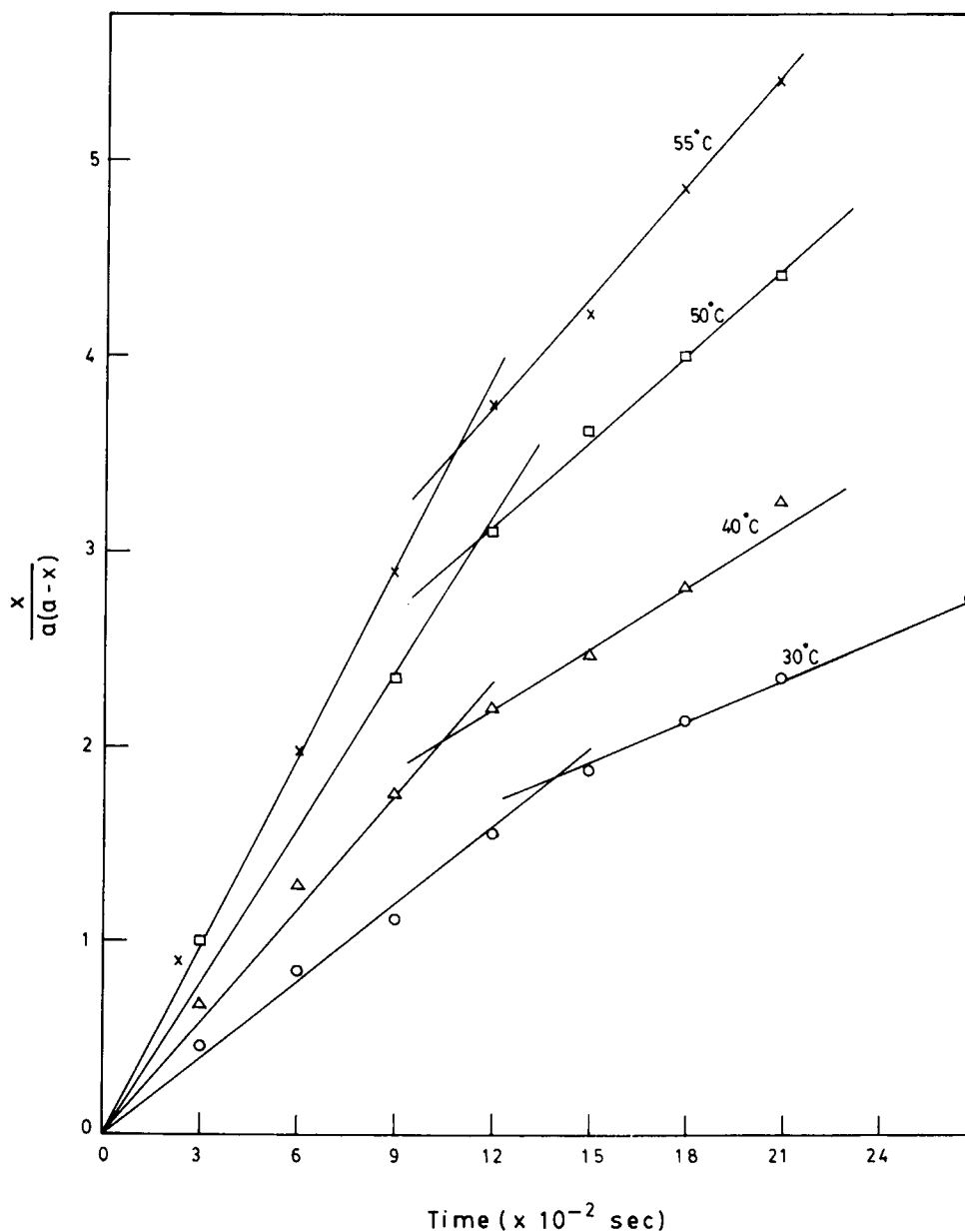


Figure 3 Dibutyltin dilaurate catalysed second-order TDI-HTPB reaction.

**Table I Second-Order Rate Constants and the Activation Parameters for the Reaction Between TDI and HTPB**

Catalyst	Temperature (°C)	$k_1 \times 10^4$	$k_2 \times 10^4$	$k_1/k_2$	Total Conversion (%)	$Ea_1$ (kJ·mol <sup>-1</sup> )	$Ea_2$ (kJ·mol <sup>-1</sup> )	$\Delta S_1^\ddagger$ (kJ <sup>-1</sup> ·mol <sup>-1</sup> )	$\Delta S_2^\ddagger$ (kJ <sup>-1</sup> ·mol <sup>-1</sup> )
		(4-NCO) (L·mol <sup>-1</sup> ·s <sup>-1</sup> )	(2-NCO) (L·mol <sup>-1</sup> ·s <sup>-1</sup> )						
NIL	30	2.272	0.555	4.093	29 (210) <sup>a</sup>				
	40	3.055	1.666	1.833	39 (210)				
	50	4.305	2.777	1.550	45 (210)	30.5	60.9	-229	-123
	55	5.555	3.872	1.434	51 (210)				
DECHA (2.5 × 10 <sup>-3</sup> M)	30	4.666	2.666	1.750	15 (35)				
	40	7.333	4.666	1.571	20 (35)	28.1	39.9	-215	-181
	50	10.330	6.666	1.549	24 (35)				
DBTDL (2.5 × 10 <sup>-4</sup> M)	55	13.330	8.333	1.599	30 (35)				
	30	13.330	6.666	2.000	36 (45)				
	40	20.000	11.000	1.818	40 (35)				
	50	25.830	15.000	1.722	47 (35)	26.1	30.2	-213	-206
	55	32.500	19.160	1.690	52 (35)				

<sup>a</sup> The values in parenthesis are time in minutes.

percent conversion is achieved within 35 min at 55°C and under the same condition 52% conversion is achieved for the dibutyltin dilaurate catalysed reaction. The rate constants for the *ortho* and *para* isocyanate groups were calculated from the slopes of the two distinct straight lines. This method is generally accepted for the reaction involving two —NCO groups present in the same benzene ring.<sup>7</sup> In the diethylcyclohexylamine catalysed reaction even with a higher catalyst concentration, the rate constants  $k_1$  and  $k_2$  for the *ortho* and *para* isocyanate groups are lower than dibutyltin dilaurate catalysed reaction. The *para* isocyanate group was four times more reactive than the *ortho* isocyanate group in the absence of the catalyst and under identical conditions of solvent and temperatures. Under identical conditions, the reactivity of the *para* isocyanate group was only twice that of the *ortho* group when

the catalyst (DECHA or DBTDL) was added. Kogen<sup>26</sup> and Tazuma and Latourette<sup>27</sup> have assumed the reactivity of the *para* isocyanate group to be ten times that of the *ortho* group and Brock<sup>28</sup> has reported a ratio of 2.67.

The effect of temperature on the less reactive isocyanate group can be understood by calculating the  $k_1/k_2$  ratios for different temperatures. As can be observed in Table I the value decreases with increasing temperature in the catalysed and uncatalysed reactions. This trend indicates that the temperature enhances the reactivity of *ortho* isocyanate group rather than the *para* group. Hence it is found that the catalysts also favour the less reactive group than the more reactive one. Although the selectivity to enhance the reactivity of the *ortho* isocyanate group is higher for diethylcyclohexylamine, Cunningham and Mastin<sup>29</sup> have observed that  $k_2$  is al-

**Table II Effect of Solvent on TDI-HTPB Reaction at 30°C**

Solvent	Dielectric Constant <sup>12</sup> ( $\epsilon$ )	DN	Hydrogen Bonding Index ( $\gamma$ )	Second Order Rate Constant	
				$k_1 \times 10^4$ (L·mol <sup>-1</sup> ·s <sup>-1</sup> )	$k_2 \times 10^4$ (L·mol <sup>-1</sup> ·s <sup>-1</sup> )
Benzene	2.28	0.1	0	2.272	0.555
Toluene	2.38	—	4.5	2.272	0.555
Chlorobenzene	5.71	0.4	1.5	1.944	1.111
Dioxane	2.21	14.8	9.7	1.770	0.770
Nitrobenzene	36.1	—	2.8	1.220	0.444

DN, Electron donor number.

ways increased more by basic catalysts (e.g., tri-*n*-butylamine) than  $k_1$  in 2,4-toluene diisocyanate 1 and 2 octanol systems.

Activation energies and entropies of activation were calculated from the slopes of the Arrhenius plots (Fig. 4) for the catalysed and uncatalysed reactions. The values of  $E_{a_1}$  (7.1 kcal/mol) and  $E_{a_2}$  (14.5 kcal/mol) corresponding to  $k_1$  and  $k_2$ , respectively, of the uncatalysed reaction are comparable with the reported values (7.5 and 11.2 kcal/mol).<sup>19</sup> The activation energy for the reaction of the

—NCO group in the 2 position is higher. This is due to the inductive and steric effects provided by neighbouring methyl substituent in the 1 position. The values of  $E_{a_1}$  and  $E_{a_2}$  for diethylcyclohexylamine and dibutyltin dilaurate catalysed reactions are reported for the first time. The activation energies for diethylcyclohexylamine catalysed reaction of *ortho* and *para* isocyanate groups are lower than those for uncatalysed reactions and higher than those for dibutyltin dilaurate catalysed reaction. The entropies of activation  $\Delta S_1^\ddagger$  and  $\Delta S_2^\ddagger$  corresponding to  $k_1$

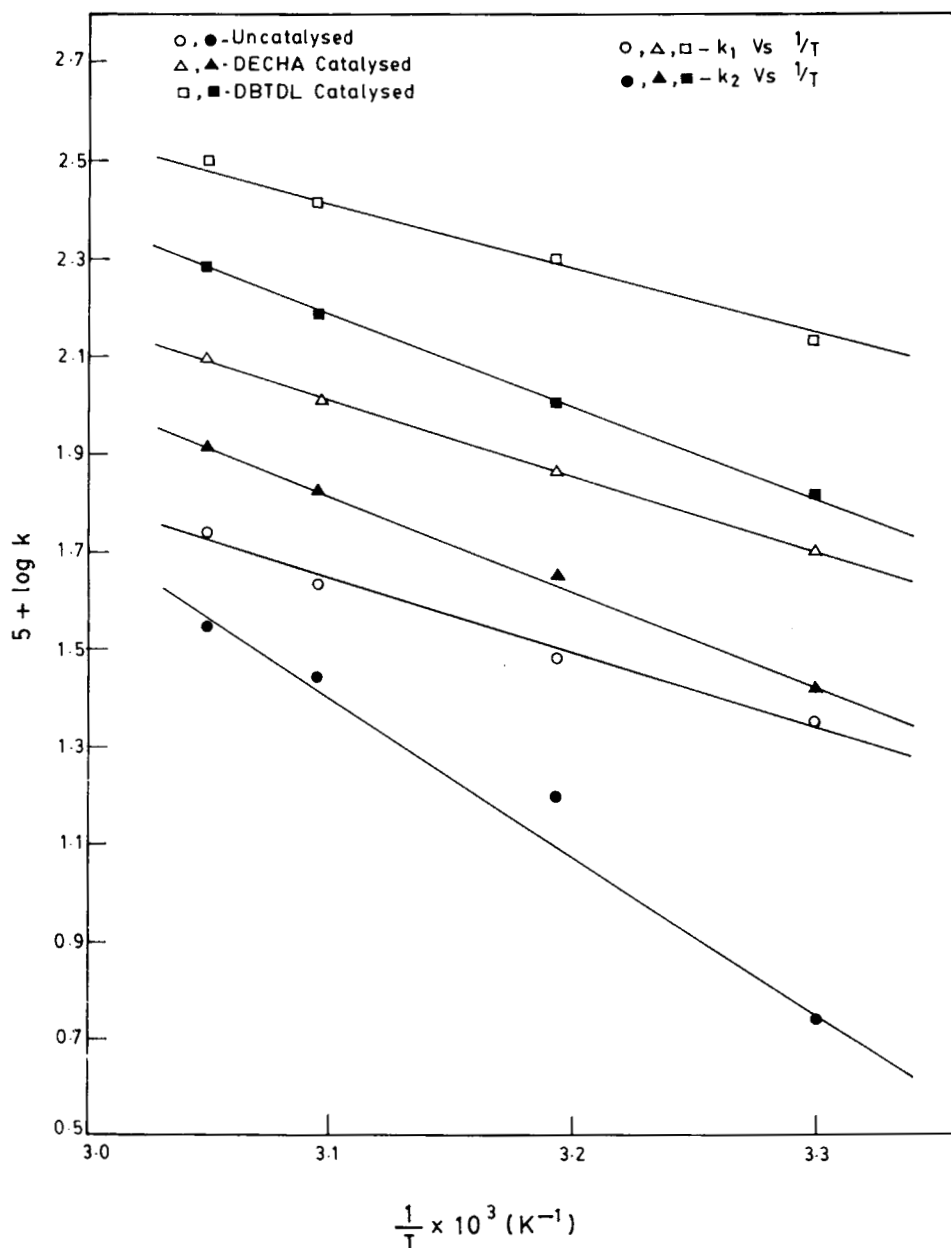


Figure 4 Arrhenius plots for second order TDI-HTPB reaction.

and  $k_2$ , respectively, of uncatalysed and catalysed reaction are highly negative due to the formation of a rigid complex in the transition state. In the catalysed reaction the difference between  $\Delta S_1^\ddagger$  and  $\Delta S_2^\ddagger$  is lower than in the uncatalysed reaction. This may be due to the activating effect of the catalyst on the *ortho* isocyanate group.

The effect of solvent on the reaction of toluene diisocyanate with HTPB was studied and the corresponding  $k_1$  and  $k_2$  values are given in the Table II. The reactivity decreased in the following order: benzene = toluene > chlorobenzene > dioxane > nitrobenzene. The dielectric constant or the electron donor number or the hydrogen bonding index of the solvents individually appear to have no effect on the rate.

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