Kinetics & Mechanism of Reaction of 4-t-Butylphenol with Formaldehyde Using Alkali Catalysts

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The rates of the individual reactions of 4-tertiarybutylphenol (4-TBP)-formaldehyde using various alkali catalysts have been measured under varying conditions of mole ratios of reactants with varying amounts of different catalysts at different temperatures. In all the experiments, the reactions were found to obey second order rate law. The experimental and the calculated value of k_0 in the case of various catalysts at 80°C have been found to agree well within the experimental errors. Entropy of activation and the thermodynamic parameters for the reactions were calculated. The relative efficiencies of the alkali catalysts followed the order:

Ca (OH)$_2$ < Ba(OH)$_2$ < NaOH < LiOH

EXTENSIVE studies have been carried[1-11] on the kinetics of the reaction of different phenols with formaldehyde. A variety of products are obtained, e.g., with simple phenol alone, two monomethylols, two dimethylols and one trimethylol and further condensation products of the interaction of methylols among themselves or with excess phenol are possible. Yeddanapalli et al.[12] made a comprehensive study on the phenol-formaldehyde reaction in the alkaline medium and reported that the reaction followed neither first nor second order.

In view of the above several disadvantages with simple phenols, it was thought of interest to make a detailed study of the reaction between 4-t-butyl-phenol and formaldehyde in alkaline medium.

Materials and Methods

4-t-Butylphenol (4-TBP) was synthesized as described by us earlier[20]. Formaldehyde (37-41% solution, BDH) containing less than 2% methanol and dioxane after purification as per the procedure of Vogel was used[21]. The catalysts LiOH, NaOH, Ba(OH)$_2$ and Ca(OH)$_2$ and NaCl, hydrated FeCl$_3$ and hydroxylamine-hydrochloride were of BDH (AR) grade. Doubly distilled water was used for preparing the solution.

The reaction was carried out in a three-necked flask fitted with a mercury seal stirrer and a reflux condenser in the temperature range 60-80° ±0.1°. In view of the insolubility of 4-TBP in water, the mixture of 4-TBP-formaldehyde was taken in 50% dioxane. Even in 50% dioxane, higher concentrations of 4-TBP were not soluble completely. Aliquots of the reaction mixture were taken at regular intervals and placed in an ice-bath to arrest the reaction. 5 ml of the aliquot mixture was used for the estimation of formaldehyde following the hydroxylamine-hydrochloride method[22] (Dioxane did not interfere in the estimation of formaldehyde). The product of the reaction, 2-methylol-4-TBP was estimated colorimetrically[23] using acid ferric chloride.

With an alkali catalyst strength (0·005 to 0·02N) and 4-TBP concentration (0·04 to 0·06M), it was found that the reaction was free from side reactions until 60% conversion. The effect of varying temperature, [catalyst] and the mole ratios of the reactants on course of the reaction was studied.

Results and Discussion

4-t-Butylphenol has two vacant ortho positions available for the addition reaction. The data could be collected on the two stages of the addition reaction by the proper choice of catalyst, type of phenol and mole ratios. Higher concentrations of alkali no doubt bring about subsequent condensation of 2-methylol-4-TBP initially formed to the dihydroxydiphenylmethane. Study was therefore limited upto 0·02N solution of alkali catalyst with the initial concentration of 4-TBP of 0·05M, thereby it was found possible to study the addition reaction up to 60%, conversion without bringing about the subsequent condensation reaction.

Under the above experimental conditions used it was found that only the first stage of the addition reaction, namely the formation of 2-methylol-4-TBP, was noticed. This was supported by the fact that the amount of 2-methylol-4-TBP formed tallied with the amount of formaldehyde consumed, thus eliminating the second stage of the reaction leading to the formation of 2,6-dimethylol-4-TBP. Since the rate of the reaction between 4-TBP and formaldehyde was found to increase above $\mu = 0·02$, in the present study, ionic strength (μ) = 0·02 was therefore kept constant throughout the work.

From the experimental results (Tables 1-3) it is clear that the reaction is of the second order. It is obvious that the substitution of t-butyl group in the para-position brings about enhanced reactivity, which is in agreement with the theoretical requirements that the introduction of an electron repelling group would be expected to increase the reactivity of the ortho- and para-positions in the substituted phenol as compared with phenol itself.

TABLE 1 — SECOND ORDER RATE CONSTANTS FOR VARIOUS ALKALI CATALYSTS AT DIFFERENT TEMPERATURES

(4-TBP=0·05M; ionic strength 0·02; HCHO=0·05M; catalyst conc.=0·006N; solvent, 50% dioxane)

Temp. (°C)	$k \times 10^4$ litre mole^{-1} sec^{-1}	Temp. (°C)	$k \times 10^4$ litre mole^{-1} sec^{-1}
LITHIUM HYDROXIDE		SODIUM HYDROXIDE	
60	2·257	60	1·778
65	3·008	65	2·231
70	4·620	70	3·379
75	5·959	75	4·962
80	8·451	70	7·134
BARIUM HYDROXIDE		CALCIUM HYDROXIDE	
60	1·486	60	1·149
65	2·067	65	1·584
70	2·953	70	2·201
75	4·423	75	3·549
80	6·941	80	4·318

TABLE 2 — SECOND ORDER RATE CONSTANTS FOR VARIOUS CONCENTRATIONS OF ALKALI CATALYSTS

(4-TBP=0·05M; ionic strength=0·02; HCHO=0·05M; temp.=80·0±0·1°; solvent, 50% dioxane)

Concentration $10^4 N$	$k \times 10^4$ (litre mole^{-1} sec^{-1})			
	LiOH	NaOH	Ba(OH)$_2$	Ca(OH)$_2$
50	8·021	5·300	4·870	4·284
60	8·450	7·121	6·941	4·31
80	10·740	8·984	8·212	5·326
100	15·99	11·194	9·527	6·329
150	20·83	13·810	10·851	7·540
200	27·43	18·25	13·675	8·147

TABLE 3 — SECOND ORDER RATE CONSTANTS FOR VARIOUS RATIOS OF REACTANTS

(Ionic strength=0·02; temp.=80·0±0·1; NaOH=0·006N; solvent 50% dioxane)

4-TBP: HCHO	$k \times 10^4$ (litre mole^{-1} sec^{-1})
2:1	6·3007
3:1	6·6233
4:1	6·656

Effect of varying temperature — The experimental rate data have been analysed as follows:

The Arrhenius energy of activation (E_a) and the frequency factor log$_{10}$ PZ have been calculated from the linear plot of log k against $1/T$.

The free energy of activation ($\Delta G^{\ddagger}$), enthalpy of activation ($\Delta H^{\ddagger}$), and the entropy of activation ($\Delta S^{\ddagger}$) have been calculated using Eq. (1)[24].

$$k = \frac{kT}{h} e^{-\Delta G^{\ddagger}/RT} = \frac{kT}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H^{\ddagger}/RT} \quad \ldots (1)$$

$\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ have also been evaluated using the relationships (2) and (3).

$$\Delta H^{\ddagger} = E_a - RT \quad \ldots (2)$$

$$\Delta S^{\ddagger} = R \ln \frac{PZ}{\ldots} \quad \ldots (3)$$

TABLE 4 — THERMODYNAMIC PARAMETERS AND FREQUENCY FACTOR AT 70°C

Catalyst	E kcal/mol	$\Delta H^{\ddagger}$ kcal/mol	$\Delta G^{\ddagger}$ kcal/mol	log$_{10}Z$	$-\Delta S^{\ddagger}$ e.u.
LiOH	15·60	14·92	25·43	6·593	30·63
NaOH	15·90	15·22	25·65	6·649	30·38
Ba(OH)$_2$	16·33	15·65	25·73	6·870	29·39
Ca(OH)$_2$	16·74	16·06	25·95	6·993	28·79

which follow from a combination of Eq. (1) with the Arrhenius equation under the assumption that E_a is temperature independent. In the direct evaluation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ from the experimental data by means of Eq. (1), $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are assumed to be temperature independent. It was found that the values of $\Delta H^{\ddagger}$ found using Eqs. (1) and (2) differ very little.

The lower values of frequency factor (Table 4) indicate that the entropy of activation ($\Delta S^{\ddagger}$) has a relatively large negative value or that the transmission coefficient was small. The latter was found to be true in a number of cases. A plot of E_a and log$_{10}$ PZ was fairly linear, but a plot of log$_{10}$ PZ against $1/E_a$ was better, as it should be on the basis of thermodynamic considerations of Fairlough and Hinshelwood[25] if both the Arrhenius parameters were the controlling factors of the reaction rate.

Effect of alkali catalysts — The 4-TBP-formaldehyde reaction could not be studied over a wider range of pH in view of the fact that increase in pH brings about very rapid condensation reaction of the methylolphenols with reactants. Hence the alkali catalyst was varied in the range $2\cdot0 \times 10^{-3}N$ to $5\cdot0 \times 10^{-3}N$ and the reaction rate constants were found to increase rapidly with increase in the concentration of the alkali (Table 2). This indicated that the phenate ion was the reactive species in the reaction. The rate of the reaction catalysed by the various catalysts followed the order Ca < Ba < Na < Li. Similar observations have been made by other workers in the case of different phenols. This observation indicates that the cation also influences the velocity of the reaction.

Effect of varying reactant concentration — The rates of individual reactions have been measured at different mole ratios of the reactants using sodium hydroxide as a catalyst. The second order rate law was obeyed in the mole ratio range 1:2, 1:3, 1:4 (formaldehyde-phenol). The rates of the reaction did not vary with changes in the mole ratios of the reactants (Table 3).

Relative contribution of alkali catalysed and uncatalysed reactions — The relative reactivities of the alkali catalysts in the phenol-formaldehyde reaction was calculated as follows. By assuming a composite mechanism for the reaction, the rate equation can be arranged as

$$-d[\text{4-TBP}\cdot\text{CH}_2\text{O}]/dt = k_u[\text{4-TBP}][\text{CH}_2\text{O}]$$
$$+ k_c[\text{4-TBP}][\text{CH}_2\text{O}][\text{catalyst}]^n \quad \ldots (4)$$

where n is the order in alkali catalyst in the catalysed part of the reaction. k_u and k_c are the rate constants for the uncatalysed and the alkali-catalysed

425

TABLE 5 — RELATIVE CONTRIBUTION OF ALKALI-CATALYSED AND UNCATALYSED REACTION

(Lithium hydroxide catalyst)

$k_u \times 10^4$ (graphic value)	k_c (litre² mole⁻²...)	[LiOH] $\times 10^4 N$	k_c[LiOH] (litre mole⁻¹ sec⁻¹)	% of catalysed reaction	$\frac{[LiOH]}{[HCHO]}$	$\left(\frac{k_c[LiOH]}{k_u}\right)$
5.0	1286	50	6.43	56.25	0.10	1.29
5.0	1286	60	7.72	60.69	0.12	1.54
5.0	1286	80	10.29	67.30	0.16	2.06
5.0	1286	100	12.86	72.00	0.20	2.57
5.0	1286	150	19.29	79.41	0.30	3.86
5.0	1286	200	25.7	83.72	0.40	5.14

reaction. The rate Eq. (4) was proposed based on two assumptions, i.e. the addition reaction is proceeding in two paths, one path is catalyst dependent and the other is catalyst independent.

$$\frac{-d(CH_2O)dt}{[4\text{-}TBP][CH_2O]} = k_u + k_c \text{ [catalyst]}^n \qquad \ldots (5)$$

$$k_0 = k_u + k_c \text{ [catalyst]}^n \qquad \ldots (6)$$

where k_0 is the observed second order rate constant. If $n = 1$, then

$$k_0 = k_u + k_c \text{ [catalyst]} \qquad \ldots (7)$$

The values of k_u and k_c were obtained from the slope and the intercept respectively of the linear plot of k_0 against [catalyst]. The values of k_0 obtained graphically from the plot of k_0 versus [catalyst] were fairly in good agreement with the values found experimentally in the absence of catalysts. The relative contribution of the alkali-catalysed and the uncatalysed parts of the 4-TBP-formaldehyde reaction have been determined using the values of k_u and k_c. The results thus obtained in the case of lithium hydroxide catalyst are given in Table 5 (similar calculations were done in the case of other catalysts also). The % of the overall reaction taking place by the catalysed path was calculated using Eq. (8).

$$\% \text{ of catalysed reaction} = \frac{k_c[\text{catalyst}]}{k_u + k_c[\text{catalyst}]} \times 100 \qquad \ldots (8)$$

The relative reactivities of the alkali-catalysed reaction of 4-TBP-formaldehyde are given in Table 6. From Table 6, it follows that the relative catalytic efficiencies of the four alkali catalysts are in the following order:

$$LiOH > NaOH > Ba(OH)_2 > Ca(OH)_2$$
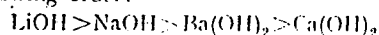
In the study of the kinetics of the phenol-formaldehyde reaction, the relative contribution of alkali-catalysed portion and the uncatalysed portion was calculated simultaneously for the first time using Eq. (7).

It has been already shown that the reaction of 4-TBP-formaldehyde under the present investigation was a bimolecular reaction, the order with respect to formaldehyde and phenate ion being one each. In addition to this, the rate of the reaction depends on [phenate ion], which is ultimately dependent alkali [catalyst]. The phenate ion is more reactive than phenol itself which may be explained on the basis of increased electron density

TABLE 6 — RELATIVE REACTIVITIES OF ALKALI-CATALYSTS

(4-TBP=0.05M; temp.=80.0±0.1°; HCHO=0.05M; solvent, 50% dioxane)

Catalyst	$k_u \times 10^4$ (litre mole⁻¹ sec⁻¹) (graphic value)	k_c (litre² mole⁻² sec⁻¹)	Relative reactivity
Ca(OH)₂	3.8	328	1.0
Ba(OH)₂	5.0	542	1.7
NaOH	4.6	804	2.5
LiOH	5.0	1286	3.9

$k_u = 4.2 \times 10^4$ litre mole⁻¹ sec⁻¹ (experimental value).

at ortho- and para-positions. The addition reaction being an aromatic substitution, the increased electron density at the ortho- and para-positions is the sum of inductive and electromeric effects acting in the same direction.

For the inductive effect, the phenate ion repels electrons while the hydroxyl group attracts electrons and hence the hydroxyl group tends to deactivate the ring. In the case of the electromeric effect, electrons are released much more rapidly by the phenate ion than by phenol alone. The overall effect of the electron displacements therefore gives the phenoxide ion having a greater reactivity than phenol. Formaldehyde reacts as $CH_2=\overset{\frown}{O}$ through the electron process, the concentration of $CH_2=\overset{\frown}{O}$ being proportional to the total formaldehyde which exists as methylene glycol in aqueous solution[26].

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