A kinetic study of reaction of 2-secbutylphenol with formaldehyde using different alkali catalysts

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The rates of reactions of 2-secbutylphenol-formaldehyde using NaOH and LiOH as catalysts at different concentrations and at different temperatures (65-80°) have been studied. The reaction obeys second order rate law. The relative efficiency of LiOH is greater than NaOH. The experimental and calculated values of k agree well within the experimental error. The energies of activation and the entropies of activation have been determined. A mechanism consistent with the kinetic data has been suggested.

Earlier workers have studied the kinetics of various phenols with formaldehyde[1] but there is no report of kinetic study on 2-secbutylphenol-formaldehyde system in presence of LiOH, taking into account the functionality of 2-secbutylphenol. It was, therefore, thought desirable to make a detailed kinetic study of the above system.

Results and Discussion

Results of the kinetic studies carried out at different temperatures and concentrations of LiOH are reported in Table 1 The overall reaction was found to obey second

order rate law. This is verified by the linear plots of $\log b$ $(na - y)/na(b - y)$ vs time (Fig. 1).

It was found that with the increase in concentration of LiOH, the energy of activation ($\Delta E^{\#}$) as well as the entropy of activation ($\Delta S^{\#}$) decrease (Table 2). The observed trend indicates that with increase in the concentration of OH^- ions, the formation of 2-secbutylphenolate ion is facilitated. As a result, the reaction becomes faster and the activation state is reached quickly. Therefore, the energy required to reach the activation state becomes lesser as observed experimentally.

Fig. 1. Plots of log [b(na - y)/na(b - y)] vs time (s) at different temperatures, [LiOH] = 17 07 × 10⁻² M

Table 1. Results of kinetic study

Initial [2-secbutylphenol] = 0 3474 M, solvent 100% methanol

Temp (±0 05)°C	Initial [HCHO] M	[LiOH] 10^2 M	Av value of k dm³ mol⁻¹ s⁻¹
65	0 3810	6 87	$(9\ 15 \pm 0\ 01) \times 10^{-6}$
	0 3780	10 04	$(1\ 58 \pm 0\ 14) \times 10^{-5}$
	0 3810	13 60	$(2.70 \pm 0\ 08) \times 10^{-5}$
	0 3775	17 07	$(4\ 37 \pm 0\ 02) \times 10^{-5}$
70	0 3778	6 87	$(1\ 27 \pm 0\ 03) \times 10^{-5}$
	0 3764	10 04	$(2\ 19 \pm 0\ 03) \times 10^{-5}$
	0 3786	13 60	$(3\ 77 \pm 0\ 05) \times 10^{-5}$
	0 3772	17 07	$(6\ 45 \pm 0\ 04) \times 10^{-5}$
75	0 3775	6 87	$(1\ 92 \pm 0\ 02) \times 10^{-5}$
	0 3782	10 04	$(3\ 38 \pm 0\ 06) \times 10^{-5}$
	0 3782	13 60	$(5\ 84 \pm 0\ 04) \times 10^{-5}$
	0 3779	17 07	$(8\ 18 \pm 0\ 05) \times 10^{-5}$
80	0 3764	6 87	$(3\ 33 \pm 0\ 04) \times 10^{-5}$
	0 3760	10 04	$(4\ 60 \pm 0\ 03) \times 10^{-5}$
	0 3759	13 60	$(7\ 92 \pm 0\ 04) \times 10^{-5}$
	0 3762	17 07	$(1\ 05 \pm 0\ 03) \times 10^{-4}$

Table 2. Activation parameters for overall reaction

[LiOH] $10^2 M$	$\Delta E^{\neq}$ kcal mol^{-1}	$\Delta S^{\neq}$ cal K^{-1} mol^{-1}
6.87	23.44	+22.03
10.04	19.53	+11.41
13.60	15.91	+2.29
17.07	11.16	-10.61

The reaction was also carried out in different solvents, viz. methanol, isopropanol and 1,4-dioxan. The rate of reaction was found to increase in the order : methanol < isopropanol < 1,4-dioxan, i.e. maximum in 1,4-dioxan which is least polar amongst the three solvents. This is attributed to the fact that 1,4-dioxan, being least polar, solvates the reacting species, the phenolate ion and the formaldehyde molecule to lesser degree as compared to more polar solvents. As a result, the reaction is faster in 1,4-dioxan.

Stepwise rate constants : The overall reaction between 2-secbutylphenol and formaldehyde proceeds according to the equation,

$$(H_5C_2)(H_3C)CHC_6H_4OH + CH_2O \xrightarrow{k}$$
$$\text{methylol derivatives} \quad (A)$$
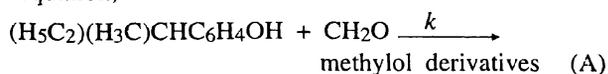
and the overall rate expression is

$$k = \frac{2.303}{t(na-b)} \log \frac{b}{na} \frac{[(na-y)]}{(b-y)}$$

where n is the functionality of 2-secbutylphenol.

In alkaline medium, the reaction however proceeds in two steps, i.e. with the formation of monomethylol and dimethylol derivatives respectively,

$$(C_2H_5)(CH_3)CH.C_6H_4OH + CH_2O \xrightarrow{k_1}$$
$$(C_2H_5)(CH_3)CH.C_6H_3OH(CH_2OH) \quad (B)$$

$$(C_2H_5)(CH_3)CH.C_6H_3OH(CH_2OH) + CH_2O \xrightarrow{k_2}$$
$$(C_2H_5)(CH_3)CH.C_6H_2OH(CH_2OH)_2 \quad (C)$$
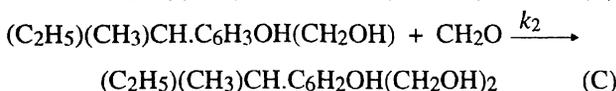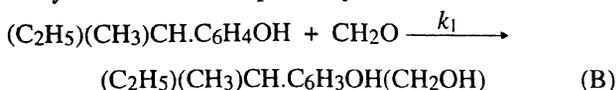
Corresponding to these equations and taking into account the functionality of 2-secbutylphenol, various kinetic equations are worked out and we obtain,

$$y = na - na^{(n-1)/n}(a - x)^{1/n} \quad (1)$$

If c represents the amount of dimethylol 2-secbutylphenol formed at any time t and u the ratio of stepwise rate constants, k_2/k_1, then

$$c = \frac{1}{1-u}\left[a - xu - a^{1-u}(a-x)^u\right] \quad (2)$$

In terms of u, y works out to be

$$y = a + x + \frac{u}{1-u}(a-x) - \frac{a^{1-u}}{1-u}(a-x)^u \quad (3)$$

On comparing eqns. (1) and (3), we obtain,

$$na - na^{(n-1)/n}(a-x)^{1/n} = a + x + \frac{u}{1-u}(a-x) - \frac{a^{1-u}}{1-u}(a-x)^u \quad (4)$$

Substituting the values of x in eqn. (4) and by using the method of successive approximation, the value of u is evaluated to be

$$u = \frac{k_2}{k_1} = 0.51$$

By utilising the value of u and the relation, $k_1 = nk$, the stepwise rate constants corresponding to the formation of mono- and dimethylol derivatives of 2-secbutylphenol are evaluated (Table 3). The concentrations of various methylol derivatives formed at any stage of the reaction were also determined (Table 4).

Table 3. Stepwise rate constants at different [LiOH] and temperatures

[LiOH] $10^2 M$	Temp. $(\pm 0.05)^\circ$C	k_1 dm^3 mol^{-1} s^{-1}	k_2 dm^3 mol^{-1} s^{-1}
6.87	65	1.81×10^{-5}	9.23×10^{-6}
10.04		3.16×10^{-5}	1.61×10^{-5}
13.60		5.40×10^{-5}	2.75×10^{-5}
17.07		9.46×10^{-5}	4.83×10^{-5}
6.87	70	2.54×10^{-5}	1.29×10^{-5}
10.04		4.38×10^{-5}	2.23×10^{-5}
13.60		7.54×10^{-5}	3.85×10^{-5}
17.07		1.29×10^{-4}	6.58×10^{-5}
6.87	75	3.84×10^{-5}	1.96×10^{-5}
10.04		6.76×10^{-5}	3.45×10^{-5}
13.60		1.17×10^{-4}	5.96×10^{-5}
17.07		1.64×10^{-4}	8.34×10^{-5}
6.87	80	6.66×10^{-5}	3.39×10^{-5}
10.04		9.20×10^{-5}	4.69×10^{-5}
13.60		1.58×10^{-4}	8.08×10^{-5}
17.07		2.10×10^{-4}	1.07×10^{-4}

Table 4. Concentration of various methylol derivatives of 2-secbutylphenol at different temperatures

[LiOH] = $13.6 \times 10^{-2} M$

Time s	Temp. $(\pm 0.05)^\circ$C	Concn. (mol dm^{-3})		
		y	x	c
3600	65	0.0247	0.0241	0.0005
7200		0.0479	0.0459	0.0016
12600		0.0755	0.0716	0.0042
18000		0.0986	0.0913	0.0170
3600	70	0.0333	0.0324	0.0009
8400		0.0714	0.0679	0.0037
13800		0.1078	0.0995	0.0091
19200		0.1354	0.1226	0.0134
3600	75	0.0494	0.0473	0.0018
7200		0.0903	0.0846	0.0061
12600		0.1376	0.1243	0.0139
19800		0.1871	0.1615	0.0255
3600	80	0.0647	0.613	0.0031
7200		0.1132	0.1038	0.0094
12600		0.1693	0.1490	0.0211
18000		0.2094	0.1775	0.0319

Effects of alkali catalysts : The 2-secbutylphenol-formaldehyde reaction was studied in presence of LiOH as well as NaOH and the reaction rate was found to be greater with LiOH. Comparison of the overall rate constants with these two catalysts is presented in Table 5. This observation indicates that cation also influences the velocity of the reaction. Also, the values of overall rate constant k were obtained from the calculated values of c, k_1 and k_2 using equation,

$$k = 1/[na - y][k_1(a - x) + k_2(x - c)]$$

and were found to be in good agreement with the experimentally obtained values of k (Table 6).

Table 5. Comparison of rate constants in presence of two catalysts LiOH and NaOH

Initial [2-secbutylphenol] = 0.347 M, initial [HCHO] = 0.3759 M, solvent : methanol, catalyst concn. = 13.6 × 10^{-2} M

Catalyst M	Time s	HCHO reacted M	$10^{-5} k$ $dm^3 mol^{-1} s^{-1}$
LiOH	3600	0.0647	7.94
	7200	0.1132	7.86
	12600	0.1693	7.95
	18000	0.2094	7.93
NaOH	3600	0.0497	5.89
	7200	0.0893	5.82
	12600	0.1386	5.91
	18000	0.1732	5.77

Table 6. Values of experimental and calculated k

[LiOH] = 13.6 × 10^{-2} M

Temp. ^0C	Average k ×10^{-5} ($dm^3 mol^{-1} s^{-1}$)	
	Exptl.	Calcd.
65	2.70 ± 0.08	2.75 ± 0.09
70	3.77 ± 0.05	3.76 ± 0.03
75	5.84 ± 0.04	5.87 ± 0.01
80	7.92 ± 0.04	7.92 ± 0.03

Mechanism : The kinetic data and the formation of methylol derivatives of 2-secbutylphenol can be rationalized by a mechanism shown in Scheme 1. Due to inductive and mesomeric effects, the electron density in 2-secbutylphenol molecule will be greater at the *ortho-* and *para*-positions with respect to the OH group. The formaldehyde molecule that has a residual positive charge at carbon and residual negative charge at oxygen on account of inductive effect, attacks the *ortho-* and *para*-position of the phenolate ion to form the activated complex (III).

The activated complex rearranges to form stable benzenoid structure (IV). This benzenoid compound reacts with water molecule forming monomethylol derivative with the regeneration of OH⁻ ion.

The monomethylol derivative further reacts with for-

$R_1 = C_2H_5$
$R_2 = CH_3$
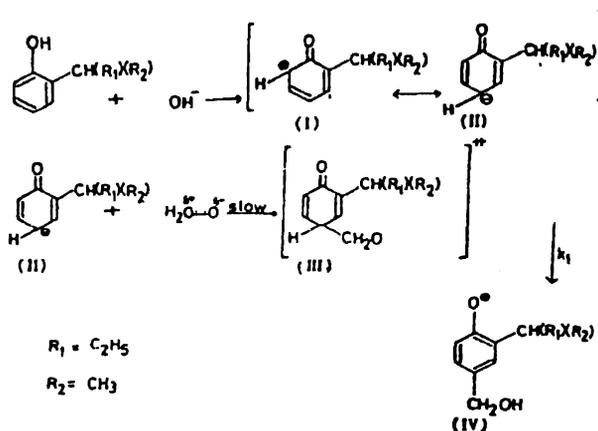
Scheme 1

maldehyde through a similar mechanism forming dimethylol-2-secbutylphenol.

According to the suggested mechanism the reaction takes place in two steps namely, the formation of 2-secbutylphenolate ion (I) and (II) and the formation of activated complex (III) and (IV). The net entropy of activation will be the sum of entropy involved in the formation of phenolate ion and the entropy required in the formation of activated complex, i.e.

$$\Delta S^{\neq}_{net} = \Delta S^{\neq}_{phenolate\ ion} + \Delta S^{\neq}_{activated\ complex}$$

The entropy of protonation is always positive, therefore, the entropy involved in the formation of 2-secbutylphenolate ion is negative and becomes more and more negative at higher alkali concentrations. However, $\Delta S^{\neq}_{activated\ complex}$ would be positive because of the formation of the unstable and disordered complex and its value is assumed to be constant. The net result would be that the entropy of activation would decrease with increase in OH⁻. This fact is reflected in the enhanced rate of reaction of formaldehyde with 2-secbutylphenol as the OH⁻ concentration increases.

Experimental

2-Secbutylphenol (Aldrich), formalin (37.5% formaldehyde), iodine, sodium hydroxide, sodium thiosulfate, potassium iodide, sodium bisulfite and potassium bromate (all B.D.H.), methanol, isopropanol and 1,4-dioxan (all Ranbaxy) were used.

A Scieno-Tech thermostat (±0.05°) was used.

Method : For alkali catalysed 2-secbutylphenol-formaldehyde reaction, solutions of 2-secbutylphenol in methanol (0.8106 M) and formaldehyde in 100% methanol (0.87–0.89 M) were prepared. Lithium hydroxide solutions of varying concentrations were also prepared. A solution of 2-secbutylphenol (15 ml) and LiOH (5 ml) of desired concentration were mixed with formaldehyde solution at the desired temperature in the thermostat. An aliquot (5 ml) of the reaction mixture was withdrawn and placed in an ice-

bath to freeze the reaction. Formaldehyde was estimated by sodium bisulfite method and 2-secbutylphenol spectrophotometrically using diazotised *p*-nitroaniline as indicator[2].

Acknowledgement

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