

Kinetics and Mechanism of Alkali-Catalyzed Reaction of 2-Methylresorcinol with Formaldehyde in Different Media

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A comprehensive kinetic and mechanistic study of 2-methylresorcinol and formaldehyde has been carried out in the temperature interval 65–80 °C using the different concentrations of sodium hydroxide as catalyst. The reaction follows an overall second-order rate law. Reaction proceeds with the formation of monomethylol 2-methylresorcinol in the first step and dimethylol 2-methylresorcinol in the second one. The overall rate constant k has been resolved into stepwise rate constants k_1 and k_2 . The mechanism of reaction, based on ΔS and ΔE values, is also proposed. Effect of changing the nature of catalyst shows that the rate of the reaction gradually increases in the order ethylamine, diethylamine, triethylamine, tetraethylammonium hydroxide and attains maximum value with sodium hydroxide. Similarly as the dielectric constant of the solvent used increases, the rate of the reaction of 2-methylresorcinol with formaldehyde also increases and it is the highest with 1,4-dioxan and lowest when methanol was employed as solvent.

Kinetic study of different phenols and formaldehyde reactions has been carried out by several workers [1–5]. Sprung and Gladstone [6] studied the condensation of saligenin with phenol and with resorcinol in the presence and in the absence of a catalyst. A review of literature reveals that not even a single kinetic study has been made on the reaction of 2-methylresorcinol with formaldehyde in relation to the functionality of 2-methylresorcinol. In the present work we have carried out 2-methylresorcinol-formaldehyde reaction at 65 °C, 70 °C, 75 °C, and 80 °C using different alkali catalysts in different media.

EXPERIMENTAL

Formaldehyde (37.5 % solution in water), potassium bromate, potassium iodide, sodium nitrate, and sodium bisulfite used were B.D.H. products. 2-Methylresorcinol used was Koch-Light (England) product and was further purified by recrystallization before use. 1,4-Dioxan and methanol were spectroscopic grade and all the other chemicals used were anal. grade or chemically pure. An immersion type thermostat MLW, model NBE (GDR) was used for rate studies and the temperature control of the thermostat was within ± 0.05 °C.

Procedure

The solution of 2-methylresorcinol was prepared in 50 % methanol. Formaldehyde solution was prepared in doubly distilled water. Reaction mixture consisting of 20 cm³ of 0.9614 mol dm⁻³ 2-methylresorcinol, 20 cm³ of formaldehyde of nearly similar concentration, and 6 cm³ of alkaline catalyst of varying concentration was taken in a round bottom flask fitted with a water condenser and suspended in the thermostat maintained at the desired temperature. After a definite interval of time, when the reaction vessel attained the temperature of the thermostat, 4 cm³ of the reaction mixture were taken out and placed in an ice bath to freeze the reaction. Formaldehyde was estimated by the usual sodium bisulfite method and 2-methylresorcinol which was separated from the reaction mixture by thin-layer chromatography, was estimated colorimetrically.

RESULTS AND DISCUSSION

The overall rate of the reaction of 2-methylresorcinol with formaldehyde in alkaline medium can be represented by the following rate equations

$$\frac{dx}{dt} = nk(a-x)(b-y) \quad (1)$$

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$$\frac{dy}{dt} = k(na - y)(b - y) \quad (2)$$

where a and b are the initial concentrations of 2-methylresorcinol and formaldehyde and x and y are the respective amounts of 2-methylresorcinol and formaldehyde reacted at time t . n is the functionality [7] of 2-methylresorcinol ($= 2$). k is the overall rate constant.

Eqn (2) on integration gives

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

Putting $n = 2$

$$k = \frac{2.303}{t(2a - b)} \log \frac{b}{2a} \frac{2a - y}{b - y} \quad (3)$$

Eqn (3) was utilized to calculate the overall rate constants at different time intervals t (Table 1). A linear dependence of $\log \left(\frac{b}{na} \frac{na - y}{b - y} \right)$ vs. time

Table 1. Overall Rate Constant k at Different Temperatures and at Different Concentrations of Sodium Hydroxide Initial [2-Methylresorcinol] = 0.418 mol dm⁻³

[NaOH] 10 ³ mol dm ⁻³	θ °C	Initial [HCHO] mol dm ⁻³	k dm ³ mol ⁻¹ s ⁻¹
4.20	65	0.4017	$(3.22 \pm 0.06) \times 10^{-6}$
10.20	65	0.4123	$(6.15 \pm 0.15) \times 10^{-6}$
16.20	65	0.4225	$(1.94 \pm 0.06) \times 10^{-5}$
22.20	65	0.4076	$(4.47 \pm 0.18) \times 10^{-5}$
4.20	70	0.4222	$(6.25 \pm 0.13) \times 10^{-6}$
10.20	70	0.4231	$(9.25 \pm 0.17) \times 10^{-6}$
16.20	70	0.4317	$(3.41 \pm 0.16) \times 10^{-5}$
22.20	70	0.4025	$(7.60 \pm 0.13) \times 10^{-5}$
4.20	75	0.4166	$(9.55 \pm 0.06) \times 10^{-6}$
10.20	75	0.4186	$(2.29 \pm 0.11) \times 10^{-5}$
16.20	75	0.4082	$(5.67 \pm 0.15) \times 10^{-5}$
22.20	75	0.4158	$(9.33 \pm 0.23) \times 10^{-5}$
4.20	80	0.4287	$(2.16 \pm 0.26) \times 10^{-5}$
10.20	80	0.4032	$(4.72 \pm 0.09) \times 10^{-5}$
16.20	80	0.4221	$(8.15 \pm 0.03) \times 10^{-5}$
22.20	80	0.4044	$(1.66 \pm 0.03) \times 10^{-4}$

confirms that the reaction follows an overall second-order rate law (Fig. 1). As the concentration of alkali catalyst increases, the rate of 2-methylresorcinol-formaldehyde reaction also increases (Fig. 2). The values

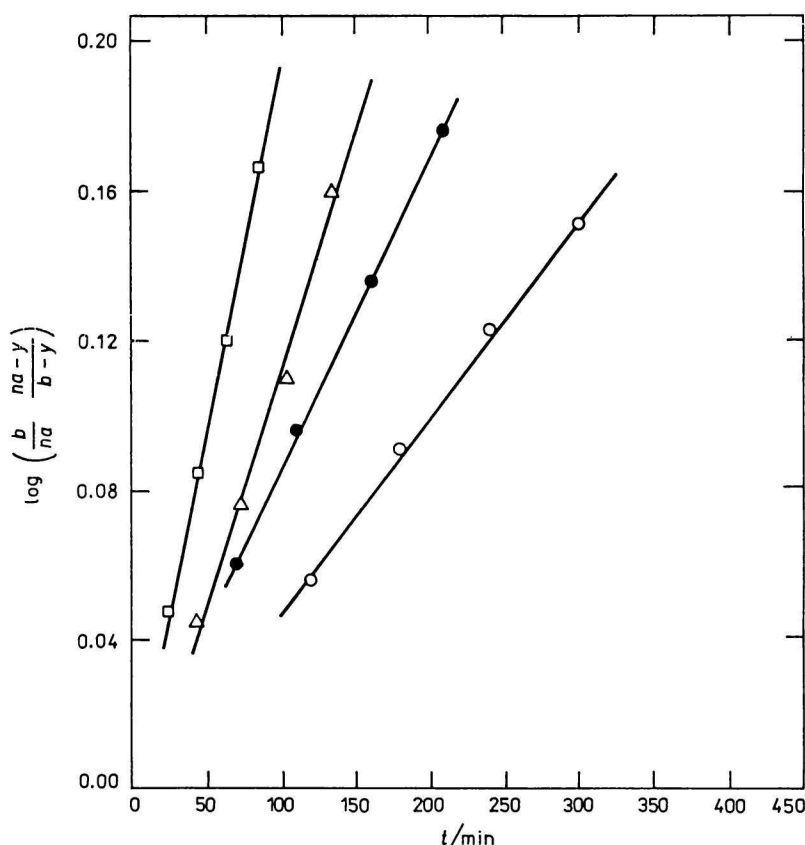


Fig. 1. A linear dependence of $\log \left(\frac{b}{na} \frac{na - y}{b - y} \right)$ vs. time confirms that the reaction follows an overall second-order rate kinetics. \circ 65 + 0.05 °C, \bullet 70 + 0.05 °C, Δ 75 + 0.05 °C, \square 80 + 0.05 °C.

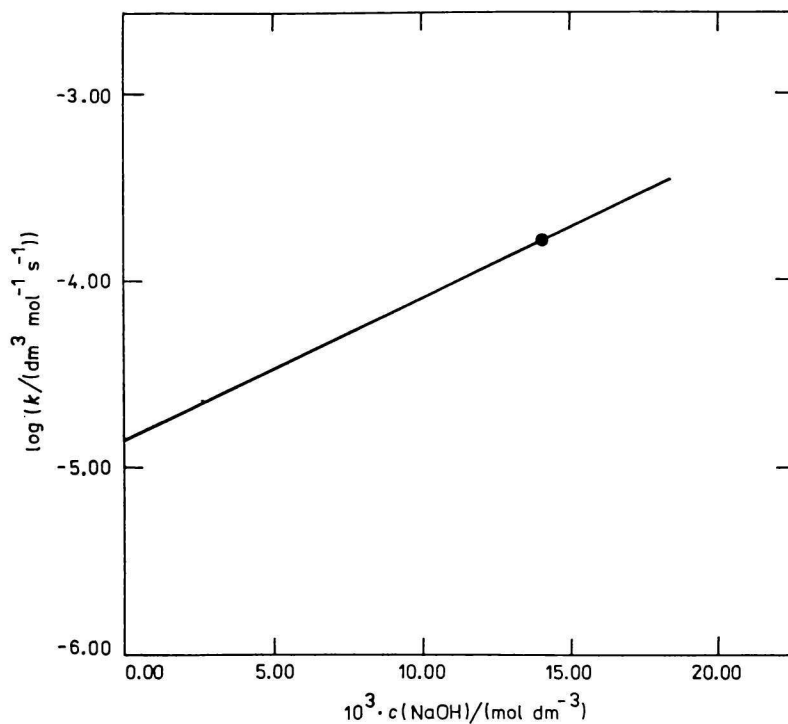


Fig. 2. As the concentration of alkali catalyst increases the second-order rate constant k value also increases. Plot of $\log \{k\}$ with alkali catalyst concentration gives a straight line.

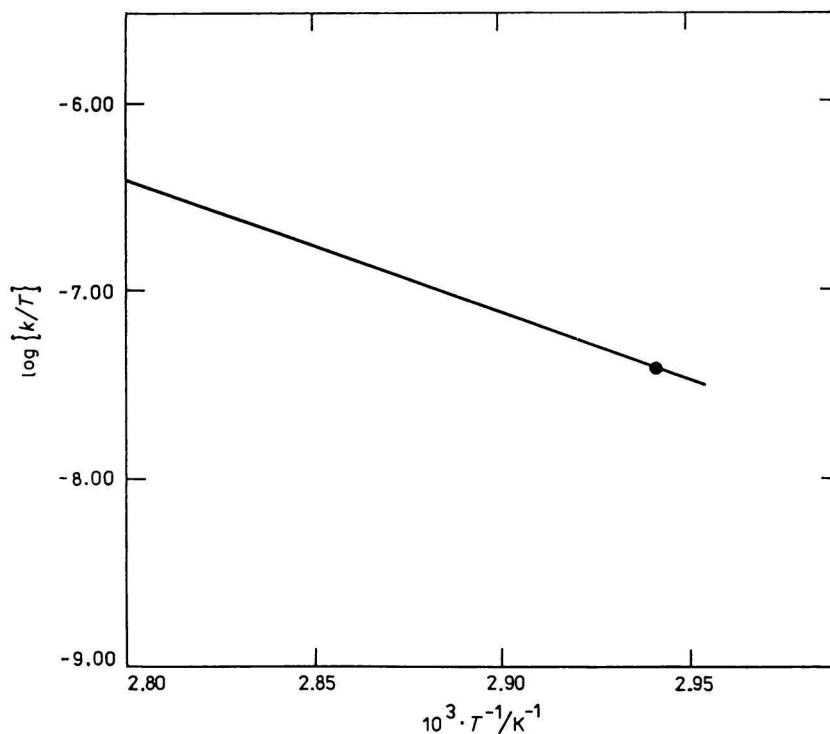


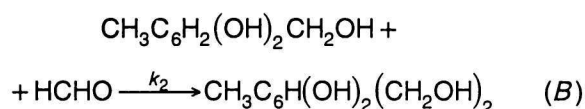
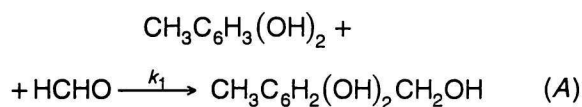
Fig. 3. Straight line with negative slope was obtained by the plot of $\log \{k/T\}$ vs. $1/T$.

Table 2. Various Activation Parameters for the 2-Methylresorcinol-Formaldehyde Reaction

[NaOH] 10 ³ mol dm ⁻³	$\Delta E \cdot 10^{-4}$ J mol ⁻¹	$\Delta S \cdot 10$ J K ⁻¹ mol ⁻¹
4.20	13.77	+ 05.52
10.20	12.85	+ 03.48
16.20	08.56	- 08.26
22.20	06.88	- 02.59

of Arrhenius parameters along with the entropies of activation were calculated by the linear plots of $\log \{k/T\}$ vs. $1/T$ (Fig. 3, Table 2).

Calculation of stepwise rate constants [8] of the reaction of 2-methylresorcinol with formaldehyde revealed that the reaction proceeds according to the step equations



The rate equations for the formation of monomethylol 2-methylresorcinol and dimethylol 2-methylresorcinol are

$$\frac{dx}{dt} = k_1(a-x)(b-y) \quad (4)$$

and

$$\frac{dc}{dt} = k_2(x-c)(b-y) \quad (5)$$

where k_1 and k_2 are the stepwise rate constants for the formation of monomethylol 2-methylresorcinol and dimethylol 2-methylresorcinol and c is the amount of monomethylol 2-methylresorcinol disappeared or the amount of dimethylol 2-methylresorcinol formed at time t .

Also,

$$\frac{dy}{dt} = \frac{dx}{dt} + \frac{dc}{dt} \quad (6)$$

Substituting the values of dx/dt and dc/dt from eqns (4) and (5) in eqn (6) we obtain

$$\frac{dy}{dt} = k_1(a-x)(b-y) + k_2(x-c)(b-y) \quad (7)$$

Dividing eqn (5) by eqn (4) and on integration

$$c = \frac{1}{1-u} \left[a - xu - a^{1-u}(a-x)^u \right] \quad (8)$$

where $u = k_2/k_1$, the ratio of the stepwise rate constants. Dividing eqn (2) by eqn (1) and integrating

$$y = na - na^{(n-1)/n} (a-x)^{1/n} \quad (9)$$

Dividing eqn (7) by eqn (4) and on integration

$$y = a + x + \frac{u(a-x)}{1-u} - \frac{a^{(1-u)}}{1-u} (a-x)^u \quad (10)$$

From eqns (9) and (10)

$$\begin{aligned} na - na^{(n-1)/n} (a-x)^{1/n} &= \\ = a + x + \frac{u}{1-u} (a-x) - \frac{a^{1-u}}{1-u} (a-x)^u &\quad (11) \end{aligned}$$

The value of u from eqn (11) was calculated by the method of successive approximation. The value of u was calculated to be

$$u = \frac{k_2}{k_1} = 0.60 \quad (12)$$

To calculate the value of k_1 dividing eqn (1) by eqn (4), we get

$$k_1 = nk \quad (13)$$

The calculated values of k_1 and k_2 are reported in Table 3.

Effect of changing the nature of the catalysts for 2-methylresorcinol-formaldehyde reaction has been stud-

Table 3. Stepwise Rate Constants at Various Alkali Concentrations and at Different Temperatures

θ °C	[NaOH] 10^3 mol dm ⁻³	Step rate constants	
		k_1 dm ³ mol ⁻¹ s ⁻¹	k_2 dm ³ mol ⁻¹ s ⁻¹
65	4.20	6.44×10^{-6}	3.86×10^{-6}
65	10.20	12.30×10^{-6}	7.38×10^{-6}
65	16.20	3.90×10^{-5}	2.34×10^{-5}
65	22.20	8.93×10^{-5}	5.36×10^{-5}
70	4.20	12.48×10^{-6}	7.49×10^{-6}
70	10.20	18.50×10^{-6}	11.10×10^{-6}
70	16.20	6.81×10^{-5}	4.08×10^{-5}
70	22.20	15.19×10^{-5}	9.17×10^{-5}
75	4.20	19.10×10^{-6}	11.46×10^{-5}
75	10.20	4.61×10^{-5}	2.76×10^{-5}
75	16.20	11.34×10^{-5}	6.80×10^{-5}
75	22.20	18.65×10^{-5}	11.18×10^{-5}
80	4.20	4.32×10^{-5}	2.59×10^{-5}
80	10.20	9.43×10^{-5}	5.68×10^{-5}
80	16.20	16.30×10^{-5}	9.78×10^{-5}
80	22.20	3.37×10^{-4}	2.03×10^{-4}

Table 4. Overall Rate Constant k Using Different Catalysts Initial [2-Methylresorcinol] = 0.418 mol dm⁻³, $\theta = 65$ °C, $c(\text{Catalyst}) = 0.0222$ mol dm⁻³

Catalyst used	Initial [HCHO]	k
	mol dm ⁻³	dm ³ mol ⁻¹ s ⁻¹
Ethylamine	0.4044	$(7.80 \pm 0.05) \times 10^{-6}$
Diethylamine	0.4285	$(1.21 \pm 0.01) \times 10^{-5}$
Triethylamine	0.4222	$(4.28 \pm 0.16) \times 10^{-5}$
Tetraethylammonium hydroxide	0.4025	$(9.31 \pm 0.20) \times 10^{-5}$

ied in the presence of a number of catalysts, *viz.* ethylamine (EA), diethylamine (DEA), triethylamine (TEA), tetraethylammonium hydroxide (TEAH), and sodium hydroxide at the concentration of 0.0222 mol dm⁻³ and at 80 °C. Rate of the reaction is maximum with sodium hydroxide and minimum in the case of ethylamine (Table 4).

The second-order rate constants for the 2-methylresorcinol-formaldehyde reaction in the presence of a number of basic catalysts could be arranged in the following decreasing order: NaOH, TEAH, TEA, DEA, EA.

Due to inductive effect, ethylamine behaves as a weaker base in comparison to tetraethylammonium hydroxide and rate of the reaction is higher in the latter case. Sodium hydroxide is a strong base and the hydroxyl ions are freely moving in the solution, so the rate of the reaction is maximum with sodium hydroxide and minimum with ethylamine.

2-Methylresorcinol-formaldehyde reaction catalyzed by 0.0222 mol dm⁻³ NaOH at a temperature of 65 °C was carried out using different solvents, *viz.* 1,4-diox-

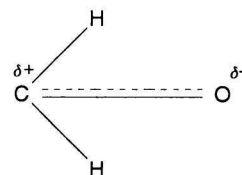
Table 5. Overall Rate Constant k in Different Media Initial [2-Methylresorcinol] = 0.418 mol dm⁻³, $\theta = 65$ °C, [Sodium Hydroxide] = 0.0222 mol dm⁻³, Organic Solvent—Water Mixture ($\varphi_r = 1$)

Organic solvent	Initial [HCHO]	k
	mol dm ⁻³	dm ³ mol ⁻¹ s ⁻¹
Methanol	0.4134	$(4.87 \pm 0.10) \times 10^{-5}$
Ethanol	0.4185	$(5.66 \pm 0.08) \times 10^{-5}$
Isopropanol	0.4046	$(7.54 \pm 0.04) \times 10^{-5}$
1,4-Dioxan	0.4126	$(8.29 \pm 0.14) \times 10^{-5}$

an, isopropanol, ethanol, and methanol at the ratio $\varphi_r = 1 : 1$ for the solvent—water mixture. Rate constant data are given in Table 5. From this table it is clear that the rate of the reaction is maximum with 1,4-dioxan and minimum with methanol as solvent. The second-order rate constants could be arranged in the following decreasing order: 1,4-dioxan, isopropanol, ethanol, methanol.

For the explanation of the mechanism it is important that due to inductive and mesomeric effects, the electron density would be greater at the *ortho* and *para* positions of 2-methylresorcinol in the presence of hydroxyl ions. Formaldehyde molecule having residual positive charge on carbon atom, attacks at the positions 4 and 6 of 2-methylresorcinolate ion to form the activated complexes I and II (Scheme 1).

The proton from the nuclear carbon atom then migrates to the oxygen of

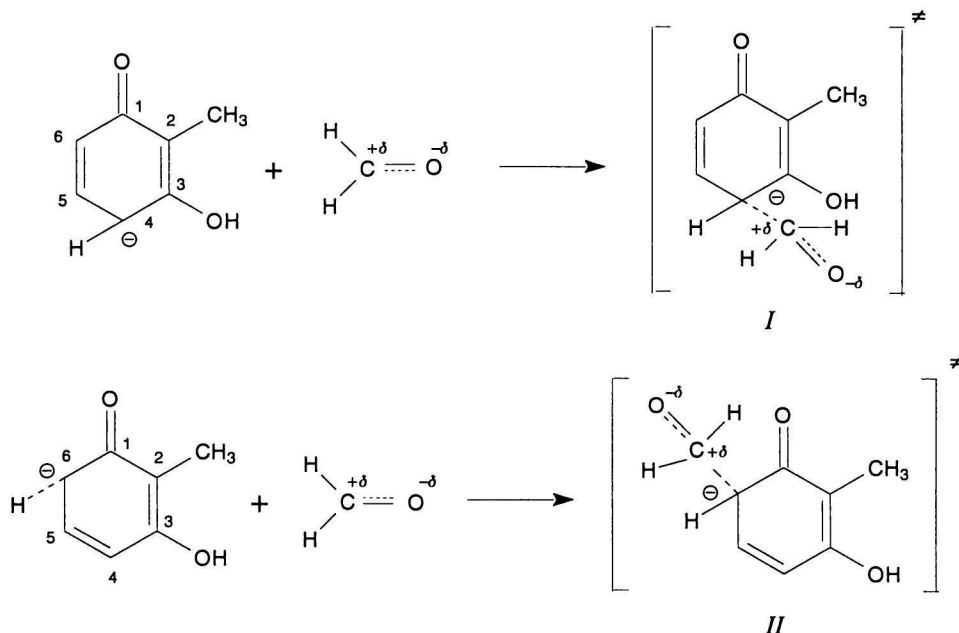


to give III and IV. Compounds III and IV (Scheme 2) react with a water molecule to give the monomethylol 2-methylresorcinols, *i.e.* 4-methylol 2-methylresorcinol and 6-methylol 2-methylresorcinol, and the regenerated OH⁻ continue to catalyze the reaction.

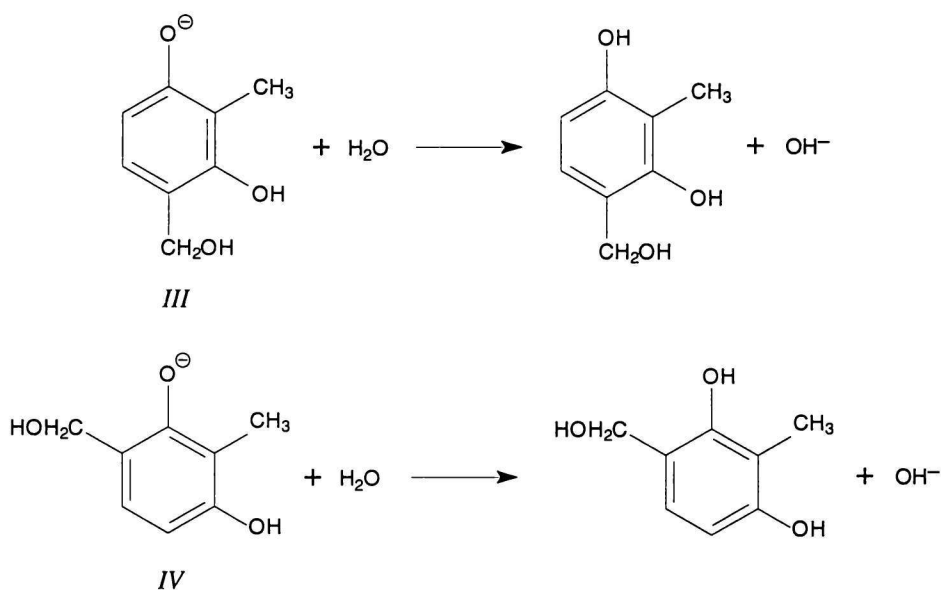
The monomethylol 2-methylresorcinol further reacts with formaldehyde molecule to give dimethylol 2-methylresorcinol through a similar mechanism.

According to the suggested mechanism for the formation of monomethylol 2-methylresorcinols (4-methylol 2-methylresorcinol and 6-methylol 2-methylresorcinol), the reaction takes place in two steps: The formation of 2-methylresorcinolate ion; the formation of activated complex I or II.

Therefore, the net entropy of activation will be the sum of the entropy required for the formation of 2-methylresorcinolate ion and for the activated complexes I and II.



Scheme 1
Activated complexes *I* and *II*.



Scheme 2
Formation of 4-methylol 2-methylresorcinol and 6-methylol 2-methylresorcinol from structure *III* and *IV*.

As the 2-methylresorcinolate ion produced is more ordered and stable in comparison to 2-methylresorcinol molecule, the entropy involved for this will be negative. Entropy in the formation of activated complex will be positive as it is disordered and unstable and its value is assumed to remain constant. The net result would be that entropy of activation would decrease with the increase in the alkali concentrations (Table 2). The smaller values of activation energy at higher concentrations of sodium hydroxide indicated that the hydroxyl ions play an important role in the reaction.

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