

ACID CATALYSED CONDESATION OF PHLOROGLUCINOL AND ACETONE-
KINETICS AND MECHANISM

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ABSTRACT

The kinetic study of the condensation reaction between phloroglucinol and acetone was investigated at 30, 35, 40 and $45 \pm 0.05^\circ \text{C}$ in 100% methanol. The hydrochloric acid concentrations used were 0.0261, 0.0364, 0.0577 and 0.0728 M. The reaction was investigated with and without a promoter, thioglycollic acid (TGA); and taking into account the functionality (n) of phloroglucinol. The reaction was found to obey a second order rate law, the rate increasing with an increase in acid catalyst concentration. The activation parameters for the overall reactions have been calculated. The reaction was also carried out in solvents 1,4-dioxane, isopropanol, ethanol and methanol. The overall rate constants were resolved into step rate constants. A mechanism consistent with the kinetic data has been suggested.

INTRODUCTION

Phenols and alkylphenols condense with carbonyl compounds in the presence of acidic and basic catalysts to form bis-phenols, which find a large number of applications in the fields of epoxy resins polycarbonates, antioxidants and in the leather industry as synthetic tanning agents.

Therefore, a comprehensive kinetic study of the reaction would no doubt give important information regarding the factors controlling the nature and properties of their products.

A thorough review of the literature reveals that comprehensive kinetic studies have been carried

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out on the reaction of phenols and substituted phenols with formaldehyde [1-5], and only a few comprehensive kinetic investigations an acid catalysed reaction of O-cresol with acetone have been investigated by Malhotra et al [6]. Not even a single kinetic study has been reported on phloroglucinol-acetone reaction, taking into account the functionality of phloroglucinol.

The reaction has been investigated at temperatures 30, 35, 40 and $45 \pm 0.05^\circ\text{C}$ and, at hydrochloric acid concentrations 0.0261, 0.0364, 0.0677 and 0.0728 M, using thioglycolic acid as a promoter.

EXPERIMENTAL

a) Materials: Phloroglucinol used was of E. Merck (Germany) product. Acetone used was of B.D.H (U.K.). Hydroxylamine hydrochloride, NaOH were also B.D.H products. Methanol used was a Glaxo (India) product. All other chemicals used were either of C.P. or A.R. grade. Phloroglucinol was recrystallized before use. An immersion type thermostat (German model NBE) was employed for the rate studies.

b) Method: Solution of phloroglucinol in methanol (0.9983 M-0.9992 M) and acetone in methanol (0.3313 M-0.3322 M) were prepared. Dry hydrochloric acid gas was bubbled for different intervals through the acetone solution before use. The dissolved hydro-

chloric acid concentration was determined by dissolving an aliquot of the solution in water and titrating against a standard solution of sodium hydroxide. The concentration of HCl was varied by adjusting the time interval for which hydrochloric acid gas was passed through the acetone solution. In a particular run, 50 ml of phloroglucinol and 50 ml of acetone solution were placed in the thermostat for a few minutes to attain the temperature of thermostat. The reaction mixture was prepared by taking 20 ml of phloroglucinol and 20 ml of acetone solutions and 2 ml of thioglycolic acid (0.084 M) in a 100 ml round bottomed flask and refluxed at desired temperature in the thermostat. After 2 or 3 minutes 5 ml of the reaction mixture was taken out and placed in an ice bath to freeze the reaction for zero reading. 2 ml of this solution was used for estimating acetone and 1 ml for the estimation of phloroglucinol. Acetone was estimated by hydroxylamine hydrochloride method and phloroglucinol was estimated spectrophotometrically using diazotized p-nitroaniline as an indicator.

RESULTS AND DISCUSSION

Results of the kinetic investigation carried out at different temperatures and acid concentrations are reported in Table 1. The overall

reaction was found to obey a second order rate law which conformed to that reported for O-cresol - acetone reaction by Malhotra et al[6] and for phenol-acetone reaction by Ghosh et al[7] and Vladmier et al[8], but differs from the result of Tokiokato [9] who observed the reaction to be 3rd order. A linear plot of $\log a/b - (b-y/a - 1.97y)$ vs time also conformed with the above factor (Fig.1). The various activation parameters for the overall rate constant were obtained from the transition state theory (Table 2).

It has been observed that energy

of activation as well as entropy of activation decreases with the increase in acid concentration, confirming the role of H^+ ion as catalyst.

The reaction was also carried out at $40 \pm 0.05^\circ C$ and 0.0577M hydrochloric acid concentration using methanol, ethanol, isopropanol and 1,4-dioxane as solvent Table 3. The rate of the reaction was found to vary in the following manner:

1,4-dioxane > isopropanol > ethanol > methanol

Such behaviour is consistent with the fact that the reaction rate decreases in the presence of water because, the

Table 1: Results of kinetic study of Phoro-glucinol Acetone reaction

[M]	Initial $[CH_3COCH_3]$ (M)	Average value of rate const $(dm^3 mol^{-1} s^{-1})$
Initial [phloroglucinol] = 0.4758 M [Promoter] = 0.004 M Temp = $30 \pm 0.05^\circ C$		
0.0261	0.1584	$(5.32 \pm 0.10) \times 10^{-5}$
0.0364	0.1578	$(1.04 \pm 0.4) \times 10^{-4}$
0.0577	0.1582	$(2.33 \pm 0.11) \times 10^{-4}$
0.0728	0.1579	$(5.28 \pm 0.05) \times 10^{-4}$
Initial [phloroglucinol] = 0.4757 M [Promoter] = 0.004 M Temp = $35 \pm 0.05^\circ C$		
0.0261	0.1584	$(1.10 \pm 0.06) \times 10^{-4}$
0.0364	0.1587	$(1.64 \pm 0.13) \times 10^{-4}$
0.0577	0.1579	$(3.26 \pm 0.11) \times 10^{-4}$
0.0728	0.1581	$(7.06 \pm 0.13) \times 10^{-4}$
Initial [phloroglucinol] = 0.4761 M [Promoter] = 0.004 M Temp = $40 \pm 0.05^\circ C$		
0.0261	0.1588	$(2.20 \pm 0.10) \times 10^{-4}$
0.0364	0.1580	$(2.92 \pm 0.07) \times 10^{-4}$
0.0577	0.1582	$(4.45 \pm 0.13) \times 10^{-4}$
0.0728	0.1579	$(8.35 \pm 0.19) \times 10^{-4}$
Initial [phloroglucinol] = 0.4754 M [Promoter] = 0.004 M Temp = $45 \pm 0.05^\circ C$		
0.0261	0.1580	$(3.47 \pm 0.06) \times 10^{-4}$
0.0364	0.1584	$(4.78 \pm 0.22) \times 10^{-4}$
0.0577	0.1581	$(6.46 \pm 0.21) \times 10^{-4}$
0.0728	0.1578	$(1.19 \pm 0.09) \times 10^{-3}$

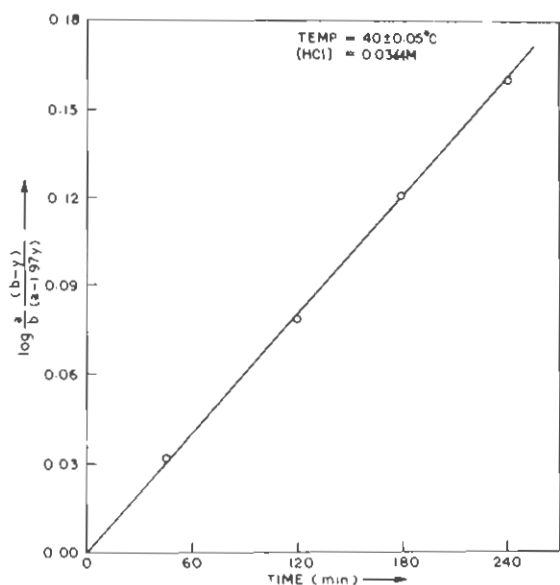


Fig.1: Plot of $\log \frac{a}{b} \left(\frac{b-y}{a-1.97y} \right)$ vs time

Table 2: Activation parameters for Phloroglucinol-Acetone reaction

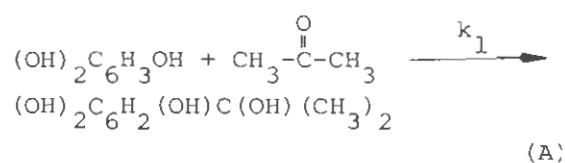
[HCl] (M)	ΔE^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal k ⁻¹ mol ⁻¹)
0.0261	25.99	7.67
0.0364	20.77	-8.28
0.0577	14.27	-28.16
0.0728	8.69	-44.57

solvent which is most polar will absorb maximum number of water molecules. With the decrease in polarity of the solvent, the rate of the reaction increases. However, the polarity of the solvent decreases with the decrease in dielectric constant of the medium (dielectric constants of methanol, isopropanol, ethanol and dioxane, respectively, are: 32.6, 18.3, 24.3 and 2.20 at 25°C). The reaction was also carried out with and without

using the promoter at temperature 45±0.05°C and the HCl concentration 0.0728 M (Table 4).

A comparative study between phloroglucinol-acetone reaction and o-cresol-acetone reaction has been made to determine the effect of substituents present in a phenol-carbonyl reaction. It has been observed that the reaction rate in the case of phloroglucinol-acetone reaction is faster than in the case of o-cresol-acetone reaction. It can be said that in the case of simple phenol, 2, 4 and 6 positions on the aromatic ring are reaction sites because the electron densities are decidedly greater at these positions due to mesomeric effect of phenolic hydroxy group. In the case of phloroglucinol all these positions are activated by the two hydroxyl groups which are present in the phloroglucinol, but in the case of o-cresol, where in the methyl group, (which is ortho - para directing group) is present in ortho position with respect to the phenolic hydroxyl group, has no effect on the reactivity of 4, 6 positions. Therefore, the rate of the reaction is less than phloroglucinol-acetone reaction.

Calculation of step rate constants:



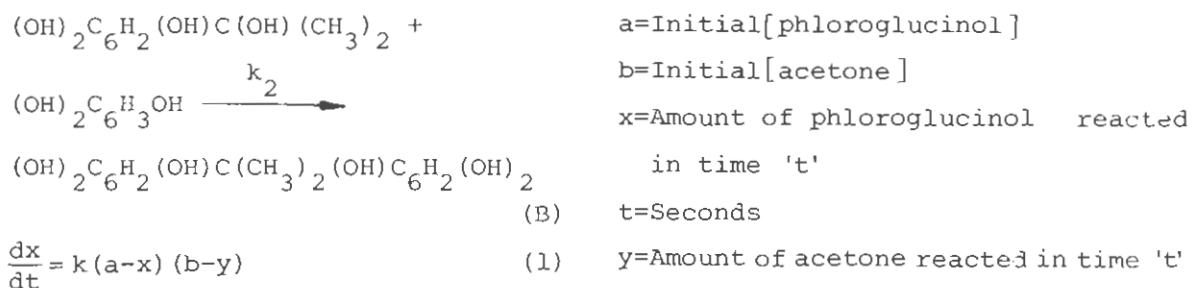


Table 3: Comparison of reactions carried out in various organic solvents

[Promoter]=0.004 M; Temp=40±0.05°C; [HCl]=0.0577 M

Solvent	Time (s)	Initial [CH ₃ COCH ₃] (M)	Initial [Phloroglucinol] (M)	[CH ₃ COCH ₃] reacted (mol dm ⁻³)	[Phloroglucinol] reacted (mol dm ⁻³)	Second order rate constant (dm ³ mol ⁻¹ s ⁻¹)	Average rate constant (dm ³ mol ⁻¹ s ⁻¹)
1,4-Dioxane	3600	0.1581	0.4757	0.0655	0.1290	6.85×10 ⁻⁴	(7.00±0.13)×10 ⁻⁴
	7200			0.0963	0.1906	7.09×10 ⁻⁴	
	10800			0.1141	0.2281	6.94×10 ⁻⁴	
	14950			0.1284	0.2553	7.13×10 ⁻⁴	
Isopropanol	3000	0.1578	0.4762	0.0451	0.0887	5.13×10 ⁻⁴	(5.11±0.08)×10 ⁻⁴
	6300			0.0741	0.1467	5.00×10 ⁻⁴	
	10800			0.1009	0.2048	5.20×10 ⁻⁴	
Ethanol	3600	0.1578	0.4759	0.0482	0.0949	4.68×10 ⁻⁴	(4.71±0.10)×10 ⁻⁴
	7200			0.0786	0.1556	4.87×10 ⁻⁴	
	9900			0.0920	0.1867	4.63×10 ⁻⁴	
	14400			0.1085	0.2137	4.67×10 ⁻⁴	
Methanol	3600	0.1582	0.4761	0.0465	0.0912	4.42×10 ⁻⁴	(4.45±0.13)×10 ⁻⁴
	6300			0.0697	0.1380	4.48×10 ⁻⁴	
	10800			0.0975	0.1809	4.30×10 ⁻⁴	
	14400			0.1084	0.2276	4.62×10 ⁻⁴	

Table 4: Comparison of the overall rate constant with and without the promoter

Temp=45±0.05°C

[HCl]=0.0728 M

Initial [CH ₃ COCH ₃] b (M)	Initial [phloroglucinol] a (M)	Time (s)	[CH ₃ COCH ₃] reacted (mol dm ⁻³)	[Phloroglucinol] reacted (mol dm ⁻³)	Second rate constant (dm ³ mol ⁻¹ s ⁻¹)	Average rate constant (dm ³ mol ⁻¹ s ⁻¹)
[Promoter]=0.004 M						
0.1578	0.4754	3600	0.0930	0.1850	1.33×10 ⁻³	(1.19±0.09)×10 ⁻³
		7200	0.1182	0.2290	1.17×10 ⁻³	
		10800	0.1327	0.2627	1.12×10 ⁻³	
		14400	0.1420	0.2837	1.16×10 ⁻³	
Without using promoter						
0.1581	0.4763	3600	0.0390	0.0776	3.53×10 ⁻⁴	(3.54±0.06)×10 ⁻⁴
		6300	0.0605	0.1197	3.62×10 ⁻⁴	
		9900	0.0789	0.1570	3.47×10 ⁻⁴	
		14400	0.0965	0.1929	3.57×10 ⁻⁴	

From equations (A) and (B) it is obvious that phloroglucinol is being used in both steps. Therefore, at any stage in the reaction the amount of phloroglucinol consumed will be more than that of acetone. This can be seen from Table 1. The average proportion of phloroglucinol and acetone reacted was actually found to be $x=1.97y$ substituting the value of x in equation (1) and on integration we get:

$$k = \frac{2.303 \times 1.97}{t(1.97b-a)} \log \frac{a}{b} \frac{(b-y)}{(a-1.97y)} \quad (2)$$

The step rate constant values

were evaluated by using the equation (3) [6]:

$$K = k_1 + k_2 \left(\frac{2y-x}{b-y} \right) \quad (3)$$

Substituting the values of x, y and k at two different time intervals, two simultaneous equations for k_1 and k_2 at a given temperature and $[HCl]$ were obtained. The values of k_1 and k_2 are reported in Table 5.

The second order rate expression has been confirmed by making a comparison of the values of the overall rate constant obtained using equation (2) with overall rate constant values

Table 5: Step rate constants at different temperatures and HCl

[HCl] (M)	K_1 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	K_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	$\frac{K_2}{K_1} = u$
Temp=30±0.05°C			
0.0261	2.81×10^{-5}	1.74×10^{-3}	61.92
0.0364	5.37×10^{-5}	3.32×10^{-3}	61.82
0.0577	1.27×10^{-4}	7.87×10^{-3}	61.96
0.0728	2.81×10^{-4}	1.7×10^{-2}	60.49
Temp=35±0.05°C			
0.0261	7.00×10^{-5}	4.34×10^{-3}	62.00
0.0364	8.53×10^{-5}	5.28×10^{-3}	61.89
0.0577	1.69×10^{-4}	1.03×10^{-2}	60.94
0.0728	3.66×10^{-4}	2.26×10^{-2}	61.74
Temp=40±0.05°C			
0.0261	1.25×10^{-4}	7.88×10^{-3}	61.44
0.0364	1.44×10^{-4}	8.96×10^{-3}	62.22
0.0577	2.20×10^{-4}	1.38×10^{-2}	62.72
0.0728	4.19×10^{-4}	2.60×10^{-2}	62.05
Temp=45±0.05°C			
0.0261	1.69×10^{-4}	1.06×10^{-2}	62.72
0.0364	2.46×10^{-4}	1.47×10^{-2}	62.28
0.0577	3.09×10^{-4}	1.93×10^{-2}	62.45
0.0728	6.13×10^{-4}	2.8×10^{-2}	61.99

as obtained purely from theoretical considerations of the reaction by using equation (4) [6] Table 6.

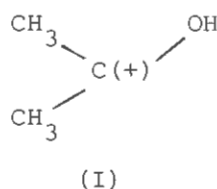
$$K = k_1 + \frac{k_2}{u-1} \left[1 + \left(\frac{b-y}{b} \right)^{u-1} \right] \quad (4)$$

Table 6: Comparison of the overall theoretical and experimental rate constants

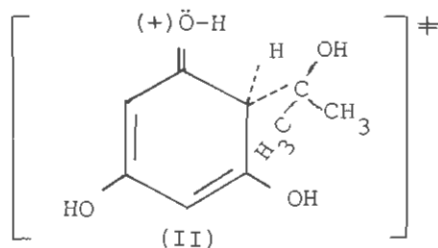
Temp ±0.05°C	[HCl] M	Average value of overall rate constants (dm ³ mol ⁻¹ s ⁻¹) × 10 ⁴	
		Experimental equation (2)	Theoretical equation (4)
35	0.0728	7.06	7.38
40	0.0728	8.35	8.44
45	0.0728	1.19	1.23

Mechanism:

In the presence of H⁺ ions, the protonation of acetone takes place, therefore, the carbonium ion (I) of acetone can exist as:

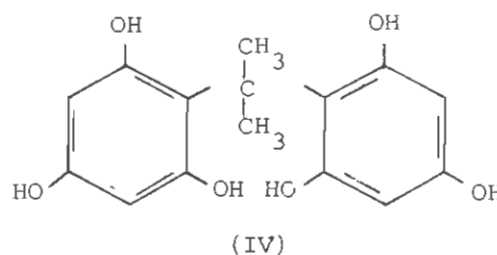
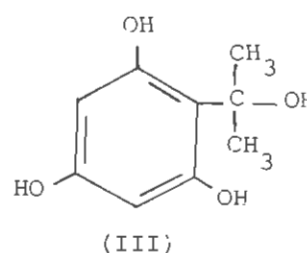


The carbonium ions of acetone react with phloroglucinol at the ortho position of phloroglucinol to form the activated complex (II):



The formation of the activated complex (II) is a slow reaction and the rate determining step. The activated

complex (II) will quickly form a stable compound of tert. alcohol derivative of phloroglucinol (III). The stable compound rearranges to form a carbonium ion in the presence of H⁺ ions by liberation of a molecule of water. This carbonium ion condenses with a molecule of phloroglucinol to form the final product (IV):



2,2'-isopropylidene bis(3,5-dihydroxyphenol)

According to mechanism suggested the formation of tert. alcohol derivative of phloroglucinol takes place in two steps:

- i) The formation of protonated acetone
 - ii) The formation of activated complex
- So the net entropy of activation will be the sum of entropy of protonation of acetone and entropy required for the formation of activated complex.

$$\Delta S_{\text{obs}}^{\ddagger} = \Delta S_{\text{p}}^{\ddagger} + \Delta S^{\ddagger}$$

The entropy of protonation is positive since protonation is acquired only at fixed sites. Because the activated complex has a more ordered molecular configuration than those of the reactant molecules, the entropy involved in the formation of activated complex (ΔS^\ddagger) would be negative and its value is assumed to remain constant. The fact that the net entropy of activation ($\Delta S_{\text{obs}}^\ddagger$) decreases with the increase in acid concentration, it indicates that at lower acid concentration, entropy of protonation ($\Delta S_{\text{p}}^\ddagger$) becomes larger than ΔS^\ddagger and this results in positive entropy of activation ($\Delta S_{\text{obs}}^\ddagger$). At higher concentration of acid, $\Delta S_{\text{p}}^\ddagger$ is invariably lower than the ΔS^\ddagger , resulting in negative entropy of activation ($\Delta S_{\text{obs}}^\ddagger$).

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