Kinetics of Alkaline-Catalyzed Cardanol–Formaldehyde Reaction. I

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Synopsis

The kinetics of reaction between cardanol and formaldehyde when catalyzed by an alkali, sodium hydroxide, has been studied and effects of process parameters, e.g., cardanol formaldehyde molal ratio, catalyst concentration, and temperature have been investigated. The addition reaction has been shown to be a second-order reaction when the concentration of active positions of reactants is used instead of their molar concentrations. Specific reaction rate constants have been determined for various cardanol–formaldehyde molal ratios, catalyst concentrations, and reaction temperatures. The energy of activation, E, is found to be 67.541 MJ/kg-mol (16.132 kcal/mol). The correlation between overall reaction rate constant and the process parameters has also been developed.

Although the reaction between cardanol, the distillate of cashew nut shell liquid (CNSL), and formaldehyde is of great importance in the manufacture of synthetic resins, there have been very few quantitative studies of the reaction kinetics involved. The investigation carried out by Bakshi and Krishnaswamy[1] on this reaction in presence of a weak basic catalyst, triethanolamine, is of a preliminary nature only. The cardanol is a naturally occurring monophenolic component of cashew nut shell liquid and may be treated as a phenol substituted by $C_{15}H_{27}$ chain at meta position. The studies reported in literature on reaction of formaldehyde and various phenols including that of Bakshi and Krishnaswamy[1] are not adaptable for the determination of reaction rate, which is an essential requirement in the design of a reactor. It was, therefore, decided to investigate the effect of various process parameters, e.g., cardanol–formaldehyde molal ratio, catalyst (NaOH) concentration, and temperature on the addition of formaldehyde to cardanol as followed by direct measurement of the uncombined formaldehyde content of the reaction mixture vs. time.

MATERIALS AND METHODS

Materials Used. Cardanol used in the experiments was obtained by direct distillation of cashew nut shell liquid. Other reagents used were formaldehyde solution—approximately 37% methanol-free, hydroxyl amine hydrochloride, sodium hydroxide, ethyl alcohol, and bromophenol solution, all of A.R. grade.

Apparatus and Procedure. The apparatus consisted of the following: (i) a three-necked flask of 1-L capacity; (ii) a condenser; (iii) a stirrer; (iv) a thermometer; (v) a vacuum sampling device; (vi) an oil bath; (vii) stoppered conical flasks.

The predetermined amounts of cardanol and formaldehyde were taken in the three-necked flask which was kept in the oil bath. The necessary accessories, e.g., condenser, stirrer, vacuum sampling device, and thermometer, were placed in their proper positions in the flask. The oil bath temperature was maintained
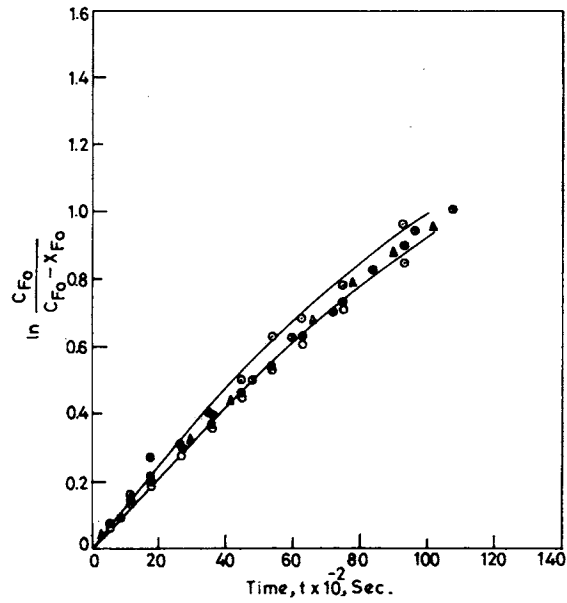
Fig. 1. Illustration of nonconformity to first-order reaction at various formaldehyde–cardanol molal ratios, $R_{F/C}$: (⊙) 0.850; (●) 1.039; (○) 1.250; (△) 1.587; (◐) 1.750. Temperature 85°C; catalyst concentration C_{NaOH}(mol/L) = 0.05165.
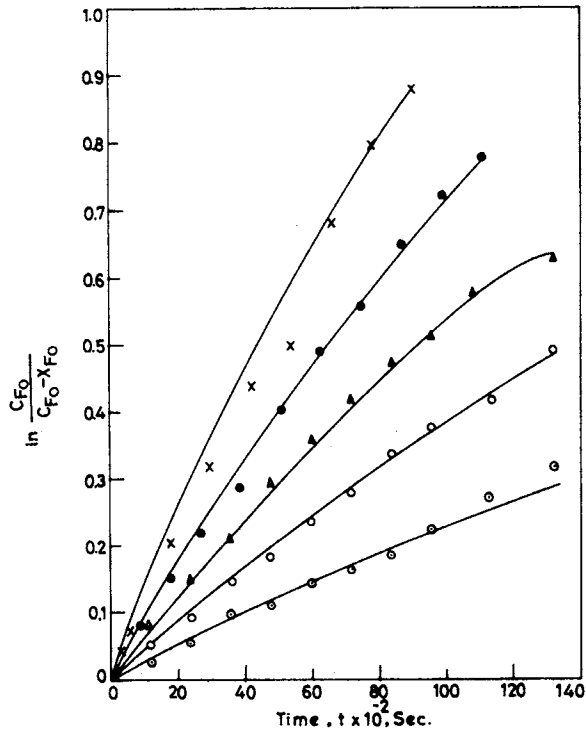

Fig. 2. Illustration of nonconformity to first-order reaction at various catalyst concentrations C_{NaOH}(mol/L): (⊙) 0.014750; (○) 0.022125; (△) 0.029500; (●) 0.036875; (✕) 0.051650. Temperature 85°C; formaldehyde–cardanol molal ratio $R_{F/C}$ = 1.587.
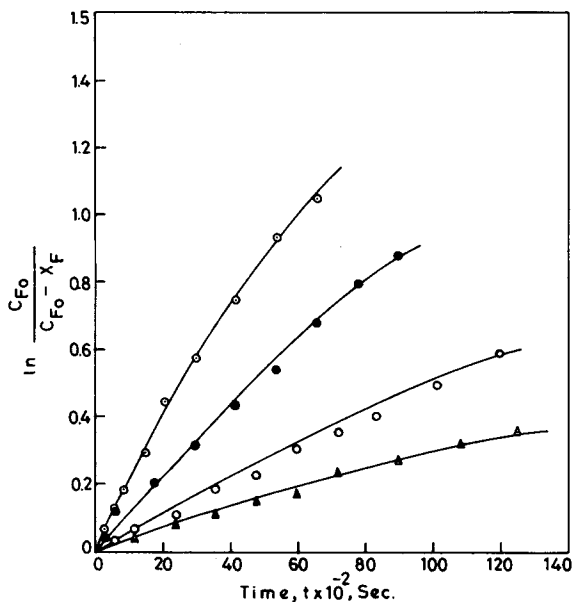
Fig. 3. Illustration of nonconformity to first-order reaction at various temperatures (°C): (⊙) 95; (●) 85; (○) 75; (▲) 65. Formaldehyde–cardanol molal ratio $R_{F/C}$ = 1.587; catalyst concentration C_{NaOH}(mol/L) = 0.05165.

at the reaction temperature. The temperature of the reaction mixture was also measured. When the temperature of the mixture was 1°C below the required temperature, the measured volume of the catalyst (NaOH) was quickly poured into the flask and the countdown was begun. The reaction being exothermic, the required temperature was attained within a few seconds. After suitable interval of time, nearly 0.50 mL reaction mixture was withdrawn by a vacuum sampling device. As the density of mixture changes significantly with time, the volumetric samples could not be taken for calculation; hence, all the samples were weighed, and the amount was recorded in each case. These samples were analyzed for free formaldehyde by the hydroxylamine hydrochloride method and formaldehyde content was calculated (mol/L reaction mixture) as follows:

$$\text{formaldehyde concentration in the sample (mol/L)} = NV\rho/S$$

where N = normality of NaOH solution, V = mL of NaOH solution of normality N used for neutralization, S = wt of the sample (g), and ρ = density of the sample (g/mL).

RESULTS AND DISCUSSION

Order of Reaction

A series of experiments were carried out with sodium hydroxide as catalyst at different process conditions, viz., formaldehyde concentration, catalyst concentration, and temperature, and experimental data thus obtained are tested for determination of order of reaction as described below.

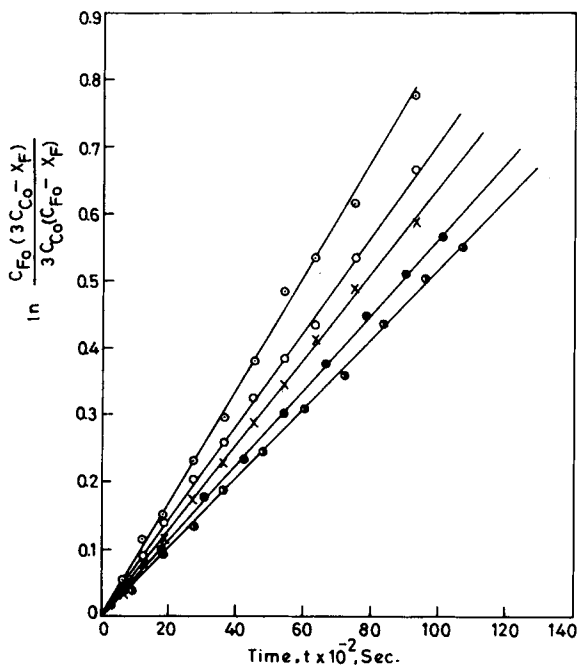The integrated rate expression for a first-order reaction is

Fig. 4. Illustration of conformity at various formaldehyde–cardanol molal ratios to second-order reaction, $R_{F/C}$: (⊙) 0.850; (O) 1.039; (×) 0.250; (●) 1.587; (◐) 1.750. Temperature 85°C; catalyst concentration C_{NaOH}(mol/L) = 0.05165.

$$\ln \frac{C_{F0}}{C_{F0} - X_F} = k \cdot t \tag{1}$$

and for a second-order reaction (the derivation is given in Appendix A) is

$$\ln \frac{C_{F0}(3C_{C0} - X_F)}{3C_{C0}(C_{F0} - X_F)} = 3(C_{C0} - C_{F0})k \cdot t \tag{2}$$

As evident from eqs. (1) and (2) a plot of $\ln C_{F0}/(C_{F0} - X_F)$ vs. time should result in a straight line when the reaction is first order and a plot of $\ln C_{F0}(3C_{C0} - X_F)/3C_{C0}(C_{F0} - X_F)$ vs. time should result in a straight line when second-order chemical reaction is involved.

Figures 1–3 show the results when the data are tested for conformity to the first-order reaction by plotting $\ln C_{F0}/(C_{F0} - X_F)$ vs. time. It is evident from these figures that the reaction at any conditions is not following a first-order scheme. $\ln C_{F0}(3C_{C0} - X_F)/3C_{C0}(C_{F0} - X_F)$ vs. t is plotted in Figures 4–6, which indicate that the reaction is following a second-order scheme at all conditions.

Nordlander[2] studied the ammonia catalyzed reaction between phenol and formaldehyde and reported the reaction to be first order. Sprung[3] studied the kinetics of reaction of various phenols and paraformaldehyde in the presence of triethanolamine catalyst and reported second-order reaction. Euler and Kispeczy[4] have also reported approximately second-order reaction between xylenols and formaldehyde. Jones[5] studied the acid-catalyzed reaction which he found to be second order. He also did some work on the base-catalyzed reaction which he believed to be first order. He did not state what catalyst was
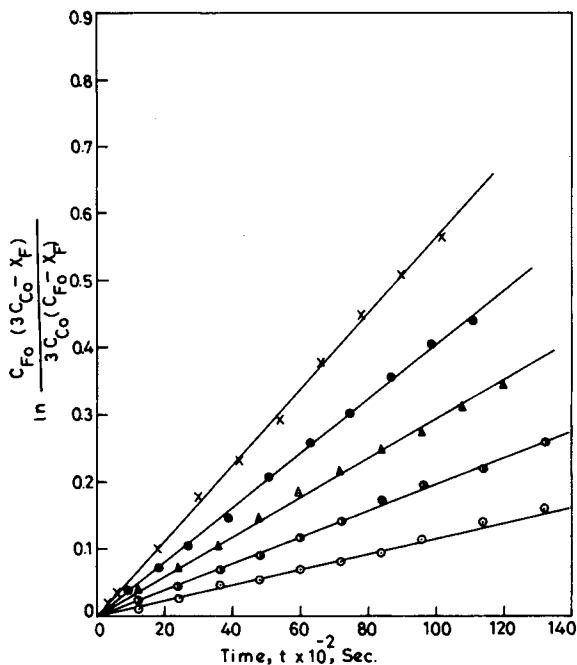
Fig. 5. Illustration of conformity at various catalyst concentrations to second-order reaction, C_{NaOH}(mol/L): (⊙) 0.014750; (◑) 0.022125; (△) 0.029500; (●) 0.036875; (×) 0.051650. Temperature 85°C; formaldehyde–cardanol molal ratio $R_{F/C}$ = 1.587.
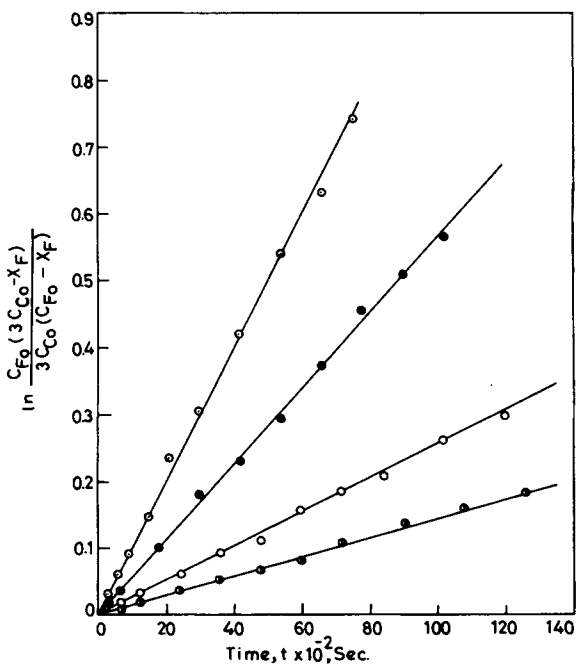

Fig. 6. Illustration of conformity at various temperatures to second-order reaction (°C): (⊙) 95; (●) 85; (○) 75; (◑) 65. Formaldehyde–cardanol molal ratio $R_{F/C}$ = 1.587; catalyst concentration C_{NaOH}(mol/L) = 0.05165.

used on the alkaline side. Debing et al.[6] carried out a comparative study of phenol–formaldehyde reaction kinetics in presence of various alkaline catalysts, e.g., ammonia as hexamethylene-tetraamine, sodium hydroxide, and substituted aliphatic amines such as monoethylamine, diethylamine, triethylamine, and tetraethyl ammonium hydroxide, and concluded that the reaction followed a first-order kinetics in the presence of hexamethylene tetraamine and a second-order kinetics in the presence of sodium hydroxide or substituted aliphatic amines when the concentrations of active positions of phenol and formaldehyde were used instead of their molar concentrations in the second-order reaction rate expression.

Bakshi and Krishnaswamy[1] studied the kinetics of the reaction of cardanol and tetrahydrocardanol with formaldehyde in the presence of triethanolamine catalyst and concluded that reactions followed the first-order scheme.

Malhotra and Avinash[7,8] also reported the reaction between phenol and formaldehyde in the presence of sodium hydroxide catalyst to follow second-order kinetics. They also used the concentration of reactive positions in terms of the functionality of phenol in the integrated rate expression. Sebenik and Lapanje[9] proposed second-order kinetics for the reaction of phenol, o-, m-, and p-cresol with formaldehyde in the presence of sodium hydroxide. Morozov et al.[10] concluded both first or second order in formaldehyde for the reaction between formaldehyde and substituted phenolic derivatives in the presence of calcium hydroxide catalyst.

From these representative works it is evident that reaction between phenols and formaldehyde in the presence of alkaline catalyst depends upon what catalyst is actually used. The reaction is a first order when weak bases such as ammonia is used as catalyst, but the overall reaction is very well represented by a second-order scheme when a strong base such as sodium hydroxide is used as a catalyst in place of ammoniacal (amines) catalyst. The present investigation on the reaction of formaldehyde with cardanol, which is a meta-substituted phenol, in the presence of sodium hydroxide as strong basic catalyst is in conformity to the above conclusion, i.e., second order.

Effect of Formaldehyde–Cardanol Molal Ratio

To study the effect of formaldehyde concentration as formaldehyde–cardanol molal ratio, the reaction between cardanol and formaldehyde was carried out at mole ratios of formaldehyde to cardanol, $R_{F/C}$ of 0.850, 1.039, 1.250, 1.587, and 1.750, at a temperature of 85°C and a catalyst concentration of 0.05165 mol NaOH/L, and the results are plotted in Figures 4 and 7. It is evident from Figure 4 that the reaction follows second-order kinetics at all formaldehyde–cardanol molal ratios. The values of overall rate constant k are determined from the slope of the straight lines obtained at different formaldehyde–cardanol molal ratio $R_{F/C}$. A plot between k and $R_{F/C}$ in Figure 7 shows that, with increase in the molal ratio, the overall second-order rate constant is increased provided that the ratio remains greater than unity. When the molal ratio of formaldehyde to cardanol is less than 1, the rate constant decreases with the increase in the concentration of formaldehyde. Thus it is concluded that the rate of reaction and thereby the rate constant decrease with increase in initial formaldehyde concentration till the molal ratio of formaldehyde to cardanol is less than unity and
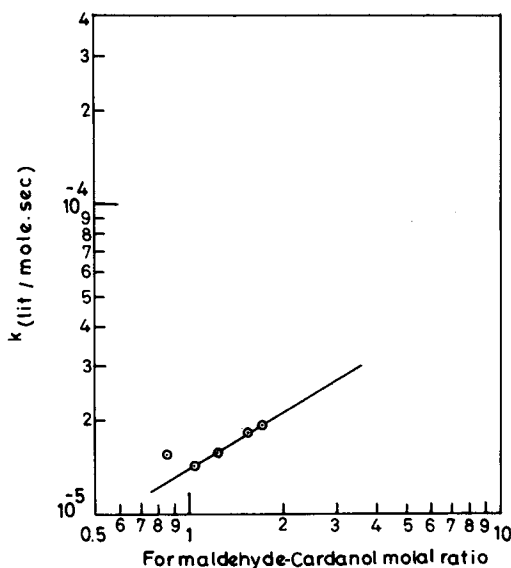
Fig. 7. Effect of formaldehyde–cardanol molal ratio on overall rate constant. Temperature 85°C; Catalyst concentration, C_{NaOH}(mol/L) = 0.05165.

increase with increase in initial formaldehyde concentration at other molal ratios higher than unity.

Malhotra and Avinash[7] and Debing et al.[6] have also reported that the reaction of phenol and formaldehyde in presence of alkaline catalyst is dependent on formaldehyde concentration. Morozov et al.[10] and Stief et al.[11] have, however, reported for the similar reaction, i.e., between formaldehyde and substituted phenolic derivatives/hydroxyl radical in presence of alkaline catalyst to be independent of formaldehyde concentration.

The present investigation supports the observations of Debing et al.[6] and Malhotra and Avinash.[7]

Effect of Catalyst Concentration

The effect of changing the concentration of catalyst from 0.01475 to 0.05165 mol/L has been shown in Figures 5 and 8 which indicate that there is a distinct effect of concentration of catalyst on the rate of reaction, which increases with the increase in catalyst concentration. The values of overall rate constant k at different NaOH concentrations are calculated from the slopes of the straight lines obtained for different catalyst concentrations in Figure 5. A log–log plot of the overall rate constant vs. catalyst concentration shown in Figure 8 reveals that the rate constant increases with increase in catalyst concentration and the relationship between these parameters can be represented by a straight line [eq. (3)].

$$k = 9.6 \times 10^{-4}(C_{NaOH})^{1.31} \tag{3}$$

Similar observations were also made by Bakshi and Krishnaswamy,[1] Debing et al.,[6] Malhotra and Avinash,[7] and several other investigators.

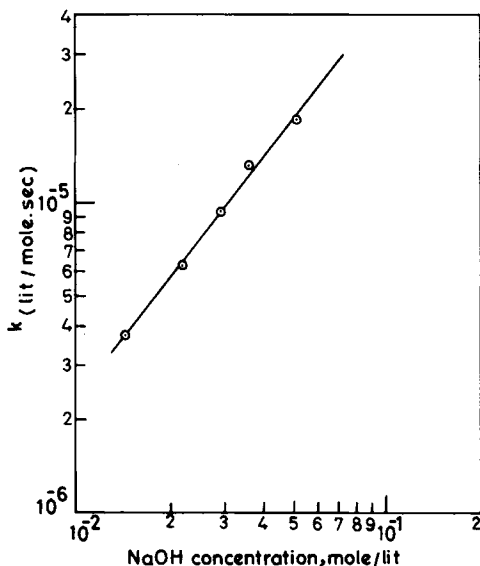Fig. 8. Effect of catalyst, NaOH, concentration on overall rate constant. Temperature 85°C; formaldehyde–cardanol molal ratio $R_{F/C}$ = 1.587.

Effect of Temperature

To determine the effect of reaction temperature on the rate of reaction between cardanol and formaldehyde, the investigation was carried out at 65°C, 75°C, 85°C, and 95°C with molal ratio of formaldehyde to cardanol of 1.587 and catalyst concentration of 0.05165 mol NaOH/L. The variation in the ratio of concentration of formaldehyde to cardanol with time taken for reaction is plotted as ln $C_{F0}(3C_{C0} - X_F)/3C_{C0}(C_{F0} - X_F)$ vs. time t in Figure 6, which confirms, as already concluded, the validity of second-order kinetics at all temperatures. The values of overall reaction constant k are calculated from the slopes of the straight lines obtained at different reaction temperature in Figure 6.

On the basis of several theories on temperature dependency of the reaction rate, e.g., Eyring theory, Arrhenius theory, collision theory, and Vant Hoff theory, an exponential relationship between reaction rate constant (k) and temperature is evident. This has been the basis for the quantitative evaluation of temperature dependency on rate of reaction.

In order to verify the validity of the Arrhenius theory to temperature dependency of reaction rate, the overall rate constants at different temperatures are plotted against the reciprocal of absolute temperatures (°K) on semilog paper, as shown in Figure 9. This figure demonstrates the validity of the theory and reveals that the rate constant increases exponentially with increasing temperature.

The Arrhenius equation can be written as

$$k = Ae^{-E/RT} \tag{4}$$

$$\log k = \log A - E/2.303RT \tag{5}$$

The energy of activation and frequency factor obtained from Figure 9 and eq. (5) are 67.541 MJ/kg-mol (16.132 kcal/mol) and 1.37 × 10⁵m³/kg-mol·s (or L/
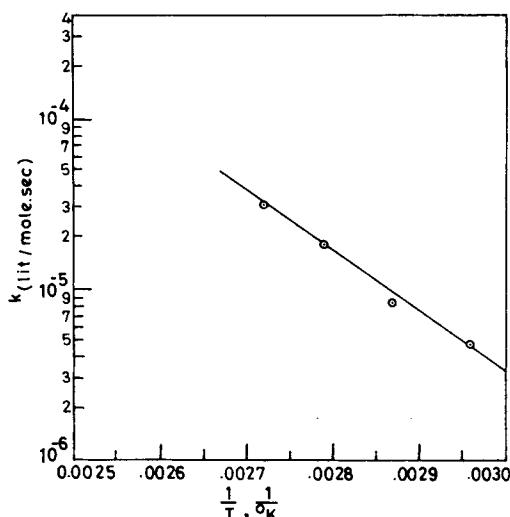
Fig. 9. Plot of overall rate constants vs. reciprocal of absolute temperatures. Formaldehyde–cardanol molal ratio $R_{F/C}$ = 1.587; catalyst concentration C_{NaOH}(mol/L) = 0.05165.

mol·s), respectively. Bakshi and Krishnaswamy[1] reported the value of activation energy equal to 51.246 MJ/kg-mol (12.24 kcal/mol) for the reaction between formaldehyde and cardanol in the presence of triethanolamine catalyst, though the reaction was reported to follow the first-order kinetics. No other information is available in the literature on the kinetics of cardanol–formaldehyde reaction with any type of catalyst. However, cardanol is also a substituted phenol, and a general comparison may be made between the present reaction and phenol–formaldehyde reaction which has been the subject of several investigators.[6,7] The value of activation energy reported by Debing et al.[6] is 87.085 MJ/kg-mol (20.8 kcal/mol), and Malhotra and Avinash[7] is 76.66 MJ/kg-mol (18.31 kcal/mol) at 10 pH of phenol–formaldehyde reaction in the presence of sodium hydroxide catalyst. The value of activation energy (E = 67.541 MJ/kg-mol) obtained in this investigation is very much in the range of the earlier reported values for the similar reaction as mentioned above.

Correlation for Overall Rate Constant

The overall rate constant for formaldehyde–cardanol reaction can be determined by eq. (2). This equation may be used to calculate overall rate constant (k) for any phenol–formaldehyde reaction provided the reaction is a second order and the functionality of phenol is 3. It is a mathematical equation and does not incorporate the effect of temperature, catalyst concentration, and molal ratio of reactants which are well known for their effects on rate constant. To incorporate these process parameters and to avoid every time experimental studies, the correlation for computation of reaction rate constant has been developed from Figures 7, 8, and 9 as follows:

$$k = 4.90 \times 10^6 \, R_{F/C}^{0.60} C_{NaOH}^{1.31} \times 10^{-3.53/T \times 10^{-3}} \qquad (6)$$

where k is overall rate constant (L/mol·s), $R_{F/C}$ is the molal ratio of formaldehyde
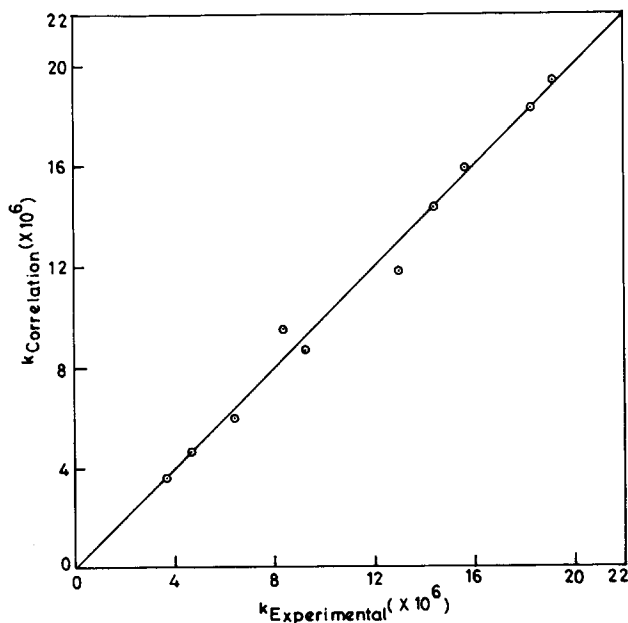
Fig. 10. Comparison between k_{exptl} and $k_{correlation}$.

to cardanol, C_{NaOH} is the concentration of NaOH (mol/L), and T is the reaction temperature (°K). This equation is valid for $R_{F/C} \geq 1$. A comparison of the experimental values of k as obtained by eq. (2) with the values calculated using eq. (6) is shown in Figure 10. The variation between the experimental and calculated values of k is within ±8%. Hence this equation may be used for calculation of rate constant for all values of $R_{F/C}$ equal to or greater than unity.

APPENDIX A: DERIVATION OF EXPRESSION FOR RATE CONSTANT FOR A SECOND-ORDER REACTION BETWEEN CARDANOL AND FORMALDEHYDE

$$C_6H_4(OH)C_{15}H_{27} + HCHO \xrightarrow{k} product$$
$$\text{cardanol} \qquad\qquad \text{formaldehyde}$$

(7)
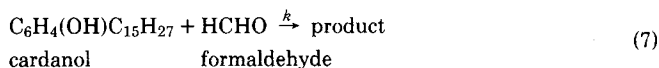
The rate of disappearance of formaldehyde, $-r_F$, is given by

$$-\frac{dC_F}{dt} = kC_F C_C$$

(8)

Let X_F = mol formaldehyde/unit volume reacted at any time. The functionality of cardanol = 3, i.e., 2 ortho and 1 para positions. Taking into considerations the concentration of reactive positions, we get

$$C_F = C_{F0} - X_F$$

(9)

$$C_C = 3C_{C0} - X_F$$

(10)

and

$$\frac{dC_F}{dt} = -\frac{dX_F}{dt}$$

(11)

Substituting eqs. (3)–(5) in eq. (2), we obtain

$$\frac{dX_F}{dt} = k(C_{F0} - X_F)(3C_{C0} - X_F) \tag{12}$$

Rearranging,

$$\frac{dX_F}{(C_{F0} - X_F)(3C_{C0} - X_F)} = kt \tag{13}$$

It is integrated by resolving into partial fractions as follows:

$$\int_0^{X_F} \left(\frac{1}{C_{F0} - 3C_{C0}}\right)\left[\frac{1}{3C_{C0} - X_F} - \frac{1}{C_{F0} - X_F}\right] dX_F = k \int_0^t t \tag{14}$$

or

$$\left(\frac{1}{C_{F0} - 3C_{C0}}\right)\left(\ln \frac{3C_{C0}}{3C_{C0} - X_F} - \ln \frac{C_{F0}}{C_{F0} - X_F}\right) = kt$$

or

$$\ln \frac{3C_{C0}(C_{F0} - X_F)}{C_{F0}(3C_{C0} - X_F)} = (C_{F0} - 3C_{C0})kt$$

or

$$\ln \frac{C_{F0}(3C_{C0} - X_F)}{3C_{C0}(C_{F0} - X_F)} = (3C_{C0} - C_{F0})kt \tag{15}$$

APPENDIX B: NOMENCLATURE

A frequency factor (*)
C cardanol
C_i molar concentration of component i (mol/L)(ML^{-3})
C_{i0} initial molar concentration of component i (mol/L)(ML^{-3})
E activation energy per mole (HM^{-1})
F formaldehyde
k reaction rate constant (*)
N normality of solution
R gas constant $L^2 \cdot T^{-2} \cdot \theta^{-1}$
$R_{F/C}$ molal ratio of formaldehyde to cardanol
r_i rate of reaction per unit volume of reactor with respect to reactant i based on formation of the reactant ($ML^{-3} \cdot T^{-1}$)
S mass of sample (g), M
T absolute temperature (°K) θ
t time (s) T
X_i moles of reactant i transformed in unit volume of reaction mixture (ML^{-3})
ρ density (g/mL)(ML^{-3})
e exponential
mol   g-mol

asterisk (*) indicates that these dimensions are dependent on order of reaction

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