

Kinetics of Alkaline-Catalyzed Cardanol-Formaldehyde Reaction. II. Mechanism of the Reaction

A. K. MISRA* and G. N. PANDEY, *Department of Chemical Engineering, H. B. Technological Institute, Kanpur- 208002, India*

Synopsis

The mechanism of the reaction between cardanol and formaldehyde when catalyzed by an alkali, sodium hydroxide, has been investigated. It was observed that only three individual rate constants, k_{11} , k_{12} , and k_{13} , out of 12 appearing in the mechanism could be quantitatively estimated due to poor separation of the intermediates. The equation for the rate of overall chemical reaction has been developed and found to agree well with the experimental data.

INTRODUCTION

Although the main utilization of cardanol is based on the production of resins by the reaction of cardanol with formaldehyde, there have been very few quantitative studies of the reaction kinetics involved. The investigation carried out by Bakshi and Krishnaswamy¹ on this reaction in presence of triethanolamine as catalyst does not deal with the mechanism of the reaction. In an earlier publication,² the effects of process parameters, e.g., molal ratio of reactants, catalyst concentration, and temperature in the production of the usual commercial resin by the reaction of cardanol with formaldehyde in the presence of sodium hydroxide have been reported. In the present investigation, the mechanism of this reaction has been presented, and the equation for the overall rate of reaction has also been developed.

MATERIALS AND METHODS

Materials Used. Cardanol used was freshly prepared by the distillation of cashew nut shell liquid. The formaldehyde used was approximately 37% solution in water and other reagents, all of A.R. grade, were hydroxylamine hydrochloride, sodium hydroxide, ethyl alcohol, and bromophenol solution.

Procedure. The reactions were carried out in an ordinary 1-L, three-necked flask equipped with a condenser, stirrer, thermometer, and vacuum sampling device. The flask was placed in an oil bath maintained at the desired temperature. The predetermined amounts of cardanol and formaldehyde in molal ratio of 1:3 were taken in the flask, and the mixture was brought to the reaction temperature. The catalyst, NaOH, solution was

* To whom correspondence should be addressed.

then added quickly, and countdown was begun. Samples were withdrawn at convenient intervals and analyzed for the free formaldehyde by the hydroxylamine hydrochloride method.³ The formaldehyde concentration in the sample, C_F , was calculated by

$$C_F(\text{mol/L}) = \frac{NV\rho}{S}$$

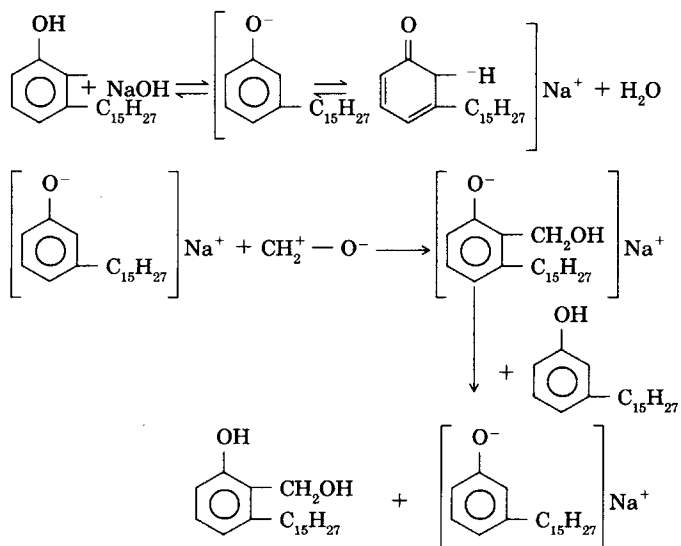
where N is the normality of NaOH solution used in the neutralization for estimation of formaldehyde, V is the volume of NaOH solution used in neutralization (mL), S is the mass of the sample (g) and ρ is the density of the sample (g/mL).

RESULTS AND DISCUSSION

Cardanol Formaldehyde Reaction Products

Cardanol-formaldehyde reaction, like a phenol formaldehyde reaction produces either thermosetting or thermoplastic resin, depending upon the catalyst used and the molal ratio of the two reactants. When the mixture contains ≥ 1 mol formaldehyde/mol cardanol, a thermosetting resin is produced irrespective of a catalyst used. The usual commercial one-step resin is obtained from a base-catalyzed reaction. When the reaction mixture contains < 1 mol formaldehyde/mol cardanol, a thermoplastic resin is produced in the absence of enough cross linking.

A novolak resin, which is a two-step thermoplastic resin, can be obtained from the acid-catalyzed reaction. In the presence of alkaline catalyst, the initial product consists of a solution of one-step resin in cardanol, when

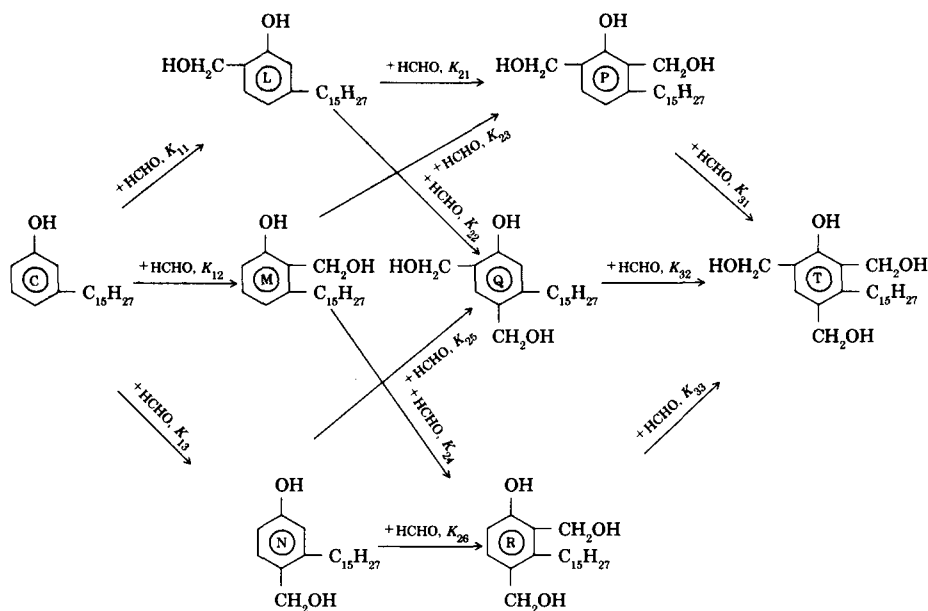


there is < 1 mol formaldehyde/mol cardanol in the mixture. This solution can be converted to a novolak upon heating without the loss of cardanol.

Mechanism of Reactions Involved in Alkaline Catalysis

The mechanism of the cardanol-formaldehyde reaction taking place in true alkaline medium depends upon the formation of the cardanol anion. This anion adds formaldehyde through a complex to form the charged methylo derivative which in turn reacts with cardanol to give methylo cardanol regenerating the anion as shown in Scheme I: The process continues till the reaction is stopped. The final composition of the resin produced depends upon the molal ratio of formaldehyde to cardanol and also the composition of cardanol as it is not a single pure compound but a mixture of phenols substituted by a long unsaturated CH chain at m positions.

When a mixture of ≥ 1 mol formaldehyde and 1 mol of cardanol are reacted, the initial reactions which are possible are shown in Scheme II: These cardanol alcohols in the mixture will also react with each other to form other complex compounds of methylene ether and diarylmethane when heating is continued and, thus, the average molecular weight of the resin increases. The extent of the reaction or the quality of the resin may be controlled by cooling the mixture at any stage.



Scheme II

Determination of Rate of Chemical Reaction

The individual rate expressions for the reactions which are possible in caustic soda catalyzed reaction as given in Scheme II, when formaldehyde/cardanol mole ratio ≥ 1 , are as follows:

$$-\frac{dC_C}{dt} = -r_C = (k_{11} + k_{12} + k_{13}) C_C C_F \quad (1)$$

$$\frac{dC_L}{dt} = k_{11} C_C C_F - (k_{21} + k_{22}) C_L C_F \quad (2)$$

$$\frac{dC_M}{dt} = k_{12} C_C C_F - (k_{23} + k_{24}) C_M C_F \quad (3)$$

$$\frac{dC_N}{dt} = k_{13} C_C C_F - (k_{25} + k_{26}) C_N C_F \quad (4)$$

$$\frac{dC_P}{dt} = k_{21} C_L C_F + k_{23} C_M C_F - k_{31} C_P C_F \quad (5)$$

$$\frac{dC_Q}{dt} = k_{22} C_L C_F + k_{25} C_N C_F - k_{32} C_Q C_F \quad (6)$$

$$\frac{dC_R}{dt} = k_{24} C_M C_F + k_{26} C_N C_F - k_{33} C_R C_F \quad (7)$$

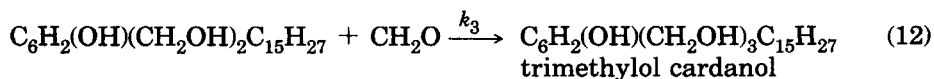
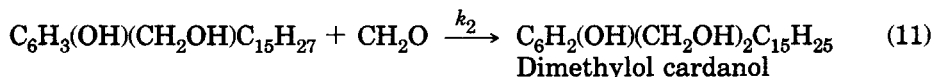
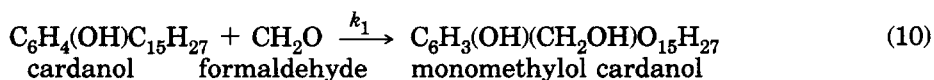
$$\frac{dC_T}{dt} = k_{31} C_P C_F + k_{32} C_Q C_F + k_{33} C_R C_F \quad (8)$$

and

$$-\frac{dC_F}{dt} = (k_{11} + k_{12} + k_{13}) C_C C_F + (k_{21} + k_{22}) C_L C_F + (k_{23} + k_{24}) C_M C_F + (k_{25} + k_{26}) C_N C_F + k_{31} C_P C_F + k_{32} C_Q C_F + k_{33} C_R C_F \quad (9)$$

These equations can be combined to develop a suitable correlation for overall rate of reaction in terms of k_{11} , k_{21} , . . . , k_{31} , etc., which may not be of practical value as the individual rate constants except k_{11} , k_{12} , and k_{13} cannot be quantitatively estimated even when very sophisticated techniques such as high performance liquid chromatography is used to determine these constants due to poor separation of the intermediates achieved. Similar observations were made by Sebenik and Lapanje⁴ in case of *m*-cresol-formaldehyde reaction. This observation would be unaffected even if the reactions involving methylene ether links and substituted methane compounds were also included in this scheme.

However, the reactions for formation of monomethylol, dimethylol, and trimethylol cardanol may be written as follows:



The reactions involve only three stepwise reaction rate constants in place of 12 as indicated earlier.

The overall reaction velocity constant k for this reaction assuming second-order kinetics is given by²

$$k = \frac{1}{(3C_{C_0} - C_{F_0})} \ln \frac{C_{F_0} (3C_{C_0} - X_F)}{3C_{C_0} (C_{F_0} - X_F)} \quad (13)$$

The rate of chemical reaction of cardanol with formaldehyde is given by

$$-r_C = \frac{dX_C}{dt} = 3k(C_{C_0} - X_C)(C_{F_0} - X_F) \quad (14)$$

$$-r_F = \frac{dX_F}{dt} = k(3C_{C_0} - X_F)(C_{F_0} - X_F) \quad (15)$$

Dividing eq. (15) by eq. (14) and integrating, we get

$$X_F = 3C_{C_0} - 3C_{C_0}^{2/3}(C_{C_0} - X_C)^{1/3} \quad (16)$$

The rate equations for the formation of monomethylol cardanol, dimethylol cardanol, and trimethylol cardanol can be written as

$$\frac{dX_C}{dt} = k_1(C_{C_0} - X_C)(C_{F_0} - X_F) \quad (17)$$

$$\frac{dX_M}{dt} = k_2(X_C - X_M)(C_{F_0} - X_F) \quad (18)$$

$$\frac{dX_D}{dt} = k_3(X_M - X_D)(C_{F_0} - X_F) \quad (19)$$

Hence, the rate of reaction in terms of disappearance rate of formaldehyde becomes

$$-r_F = \frac{dX_F}{dt} = \frac{dX_C}{dt} + \frac{dX_M}{dt} + \frac{dX_D}{dt} \quad (20)$$

or

$$-r_F = k(C_{C_0} - X_C)(C_{F_0} - X_F) + k_2(X_C - X_M)(C_{F_0} - X_F) + k_3(X_M - X_D)(C_{F_0} - X_F) \quad (21)$$

Equation (21) enables us to calculate the theoretical rate of reaction when k_1 , k_2 , k_3 , X_C , X_M , X_D , and initial concentrations of cardanol and formaldehyde are known. For this, eqs. (17)–(19) are solved. The boundary conditions needed for the solution are

$$\begin{aligned}
 X_F &= 0 \\
 X_C &= 0 \\
 X_M &= 0 \quad \text{at } t = 0 \\
 X_D &= 0
 \end{aligned}
 \tag{22}$$

Solving eqs. (17)–(19) with the boundary conditions given in eq. (22), the expressions obtained for disappearance of monomethylol cardanol and dimethylol cardanol are as follows:

$$X_M = \frac{1}{1 - k_2/k_1} \left[C_{C0} - X_C \frac{k_2}{k_1} - C_{C0}^{1-k_2/k_1} (C_{C0} - X_C)^{k_2/k_1} \right]
 \tag{23}$$

$$\begin{aligned}
 X_D &= \frac{k_3/k_1}{1 - k_2/k_1} \left[\frac{1 - k_2/k_1}{k_3/k_1} C_{C0} - \frac{k_2/k_1}{1 - k_3/k_1} (C_{C0} - X_C) \right. \\
 &\quad \left. + \frac{C_{C0}^{1-k_2/k_1} (C_{C0} - X_C)^{k_2/k_1}}{k_2/k_1 - k_3/k_1} \right] \\
 &\quad - \frac{(k_2/k_1) C_{C0}^{1-k_3/k_1}}{(1 - k_3/k_1)(k_2/k_1 - k_3/k_1)} (C_{C0} - X_C)^{k_3/k_1}
 \end{aligned}
 \tag{24}$$

and the expression for calculating the stepwise rate constants is obtained as

$$\begin{aligned}
 X_F &= 2C_{C0} + X_C - \frac{(k_2/k_1) C_{C0}^{1-k_3/k_1} (C_{C0} - X_C)^{k_3/k_1}}{(1 - k_3/k_1)(k_2/k_1 - k_3/k_1)} \\
 &\quad - \frac{(k_2/k_1 - 2k_3/k_1) C_{C0}^{1-k_2/k_1}}{(k_2/k_1 - k_3/k_1)(1 - k_2/k_1)} (C_{C0} - X_C)^{k_2/k_1} \\
 &\quad + \frac{(k_2/k_1)(1 - 2k_3/k_1)}{(1 - k_2/k_1)(1 - k_3/k_1)} (C_{C0} - X_C)
 \end{aligned}
 \tag{25}$$

The detailed mathematical derivations are given elsewhere.⁵

The values of k_2/k_1 are first determined by putting $k_3 = 0$ in eq. (25) as reaction (12) does not take place in the beginning due to consecutive nature of the reaction. Substituting the average value of k_2/k_1 in eq. (25), k_3/k_1 is calculated. Finally the average value of k_3/k_1 is determined. The values thus obtained are as follows:

$$\frac{k_2}{k_1} = 0.74
 \tag{26}$$

$$\frac{k_3}{k_1} = 0.22
 \tag{27}$$

and, from eqs. (14) and (17),

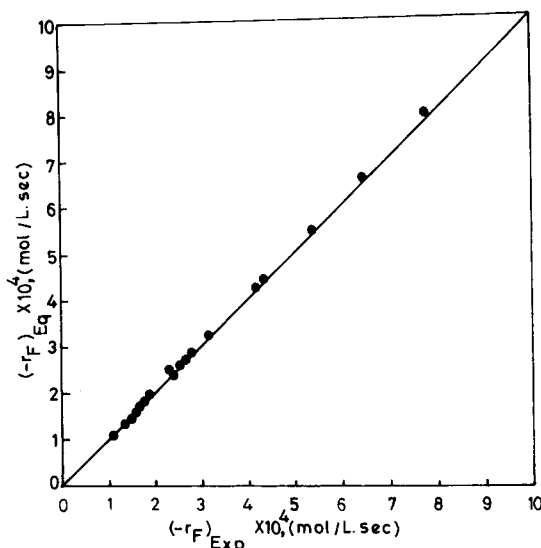


Fig. 1. Comparison between experimental and theoretical rate of reaction.

$$\frac{k_1}{k} = 3 \quad (28)$$

The programme used for evaluating k_2/k_1 and k_3/k_1 for average values of k_2/k_1 is given in Appendix A.

It is evident by the above discussion that the values of X_C , X_M , X_D , k_1 , k_2 , and k_3 could be calculated for known values of X_C by using eqs. (16), (23), (24), and (26)–(28). The rate of the chemical reaction in terms of the rate of disappearance of formaldehyde is obtained by substituting these values in eq. (21) as follows:

$$-r_F = (C_{F0} - X_F)[k_1(C_{C0} - X_C) + k_2(X_C - X_M) + k_3(X_M - X_D)] \quad (29)$$

Comparison with Experimental Rate

For comparison the values of reaction rate obtained experimentally using eq. (15) are plotted against the calculated values using eq. (29) as shown in Figure 1. It is evident from the figure that about 80% of the data points are in excellent agreement with the calculated values without practically any deviation. However, a little variation was observed in some cases: 10% of the data points are within $\pm 2\%$ while the remaining 10% are within $\pm 5\%$ deviation. Hence, this equation could be used for design purposes.

APPENDIX A

Computer Program for Calculation of Ratios of Stepwise Rate Constants k_2/k_1 and k_3/k_1

C CARDANOL-FORMALDEHYDE REACTION
 C N = FUNCTIONALITY OF CARDANOL
 C A = INITIAL CONCENTRATION OF CARDANOL

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C      X = AMOUNT OF CARDANOL DISAPPEARED AT ANY TIME
C      U = K2/K1
C      V = K3/K1
C      Y = AMOUNT OF FORMALDEHYDE DISAPPEARED AT ANY TIME
COMMON/AREA1/N,A,X,Y
      READ 10,M
      READ 10,N,A
      TYPE 20,N,A
300    CONTINUE
      MM=MM+1
      IF(MM.GT.M) STOP
      READ 90,Y
      TYPE 215,Y
      READ 30,U1,U2
      TYPE 40,U1,U2
      READ 30,V1,V2
      TYPE 50,V1,V2
      X=A+((Y-N*A)**N)/((N**N)*(A**(N-1.)))
      TYPE 80,X
      U3=0.75
      GO TO 100
      CALL FV(U1,0.0,F1)
110    CALL FV(U2,0.0,F2)
      U3=(U1*F2-U2*F1)/(F2-F1)
      IF (ABS(U3-U2).LT.0.001) GO TO 100
      U1=U2
      U2=U3
      F1=F2
      GOTO 110
100    TYPE 60,U3
      CALL FV(U3,V1,F1)
130    CALL FV(U3,V2,F2)
      V3=(V1*F2-V2*F1)/(F2-F1)
      IF (ABS(V3-V2).LT.0.001) GO TO 120
      V1=V2
      V2=V3
      F1=F2
      GOTO 130
120    TYPE 70,V3
      GO TO 300
10      FORMAT(I2,2F6.4)
20      FORMAT(10X,'N=',I2,5X,',A=',F6.4)
30      FORMAT(2F4.2)
40      FORMAT(10X,'U1=',F4.2,5X,',U2=',F4.2)
50      FORMAT(10X,'V1=',F4.2,5X,',V2=',F4.2)
60      FORMAT(10X,'THE VALUE OF U IS ',F8.6)
70      FORMAT(10X,'THE VALUE OF V IS ',F16.8)
      STOP
80      FORMAT(10X,'THE VALUE OF X IS ',F16.8)
90      FORMAT(F5.3)
215    FORMAT(10X,'THE VALUE OF Y IS ',F8.6)
      END
      SUBROUTINE FV(U,V,F)
COMMON/AREA1/N,A,X,Y
      Y1=(U*(1.0-2.0*V)*(A-X))/((1.0-U)*(1.0-V))
      Y2=((U-2.0*V)*(A**(1.0-U))*((A-X)**U))/((1.0-U)*(U-V))
      Y3=(U*(A**(1.0-V))*((A-X)**V))/((1.0-V)*(U-V))
      F=Y-2.0*A-X-Y1+Y2+Y3
      RETURN
      END

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APPENDIX B

Nomenclature

C	cardanol
C_i	molar concentration of i in the mixture at any time (mol/L)
C_{i0}	initial molar concentration of reactant i (mol/L)
D	dimethylol cardanol
F	formaldehyde
k	overall second order reaction rate constant (L/mol · s)
k_1, k_2, k_3	stepwise rate constants (L/mol · s)
k_{11}, k_{12}, k_{13}	rate constants for first, second, and third second-order reactions between cardanol and formaldehyde as shown in Scheme II (L/mol · s)
k_{21}, k_{22}, k_{23}	rate constants for first, second, and third second-order reactions between monomethylol cardanol and formaldehyde as shown in Scheme II (L/mol · s)
k_{31}, k_{32}, k_{33}	rate constants for first, second and third second-order reaction between dimethylol cardanol and formaldehyde as shown in Scheme II.
L,M,N	monomethylol cardanols as in Scheme II
M	monomethylol cardanol
N	normality of NaOH solution used in the neutralization for estimation of formaldehyde
P,Q,R	dimethylol cardanols as in Scheme II
r_i	rate of chemical reaction per unit volume of reactor with respect to reactant i based on the formation of the reactant (mol/L · s)
S	mass of a sample (g)
T	trimethylol cardanol
t	time (s)
V	volume of NaOH solution used for neutralization (mL)
X_i	moles of reactant i transformed in unit volume of reaction mixture (mol/L)
ρ	density of the sample (g/mL)

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