Kinetics of Alkaline-Catalyzed Cardanol–Formaldehyde Reaction. III. Determination of Composition of the Resin

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Synopsis

In the present study, a quick method for the determination of composition of the resin formed by alkaline-catalyzed cardanol–formaldehyde reaction has been suggested. The complete analysis of the product could be carried out by determining experimentally the concentration of only one reactant, viz., formaldehyde present in the reaction mixture at any time.

INTRODUCTION

The utilization of cardanol is mainly based on the production of a resin by cardanol–formaldehyde reaction. The properties of a resin, e.g., solubility, density, flexibility, etc., depend upon its molecular weight, which in turn depends upon the final composition of the resin.

In the kinetic study of the alkaline-catalyzed cardanol–formaldehyde reaction, the effects of various process parameters have already been investigated.[1] The same study has now been extended to the determination of the composition of the product.

EXPERIMENTAL

The experimental setup and the procedure were same as described in an earlier publication.[1] The cardanol and formaldehyde were taken in the molal ratio of 1:3 in the flask. The count down was begun from the time of addition of NaOH solution. The catalyst (NaOH) concentration in this experiment was 0.0295 mol/L and the temperature 85°C. The samples withdrawn by a vacuum sampling device were analyzed for free formaldehyde and its concentration reported in mol/L of mixture.

DISCUSSION

Calculation Method

In cardanol formaldehyde reaction, the formation of mono-, di-, and trimethylol cardanol can be written as follows:

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$$C_6H_4(OH)C_{15}H_{27} + CH_2O \xrightarrow{k_1} C_6H_3(OH)(CH_2OH)C_{15}H_{27} \tag{1}$$
cardanol formaldehyde monomethylol cardanol

$$C_6H_3(OH)(CH_2OH)_{15}H_{27} + CH_2O \xrightarrow{k_2} C_6H_2(OH)(CH_2OH)_2C_{15}H_{27} \tag{2}$$
dimethylol cardanol

$$C_6H_2(OH)(CH_2OH)_2C_{15}H_{27} + CH_2O \xrightarrow{k_3} C_6H(OH)(CH_2OH)_3C_{15}H_{27} \tag{3}$$
trimethylol cardanol

and the over all reaction is

$$\text{cardanol} + \text{formaldehyde} \xrightarrow{k} \text{product} \tag{4}$$

The overall reaction rate constant k for this reaction using second-order kinetics is given by[1]

$$k = \left(\frac{1}{3C_{C0} - C_{F0}}\right) \ln \frac{C_{F0}}{3C_{C0}} \left(\frac{3C_{C0} - X_F}{C_{F0} - X_F}\right) \tag{5}$$

Equations for rate of reaction are

$$-r_C = \frac{dX_C}{dt} = 3k(C_{C0} - X_C)(C_{F0} - X_F) \tag{6}$$

and

$$-r_F = \frac{dX_F}{dt} = k(3C_{C0} - X_F)(C_{F0} - X_F) \tag{7}$$

Dividing eq. (7) by eq. (6), we get

$$\frac{dX_F}{dX_C} = \frac{(3C_{C0} - X_F)}{3(C_{C0} - X_C)} \tag{8}$$

Separating the variables and integrating, we get

$$X_F = 3C_{C0} - 3C_{C0}^{2/3}(C_{C0} - X_C)^{1/3} \tag{9}$$

It has already been shown[2] that the rate equations for the formation of mono-, di-, and trimethylol cardanol according to eqs. (1)–(3) when integrated with proper boundary conditions yielded the following expressions for X_M and X_D:

$$X_M = \frac{1}{1 - k_2/k_1}\left[C_{C0} - \frac{k_2}{k_1}X_C - C_{C0}^{1-k_2/k_1}(C_{C0} - X_C)^{k_2/k_1}\right] \tag{10}$$

$$X_D = \frac{k_3/k_1}{1 - k_2/k_1}\left[\left(\frac{1 - k_2/k_1}{k_3/k_1}\right)C_{C0} - \frac{k_2/k_1}{1 - k_3/k_1}(C_{C0} - X_C) + \frac{C_{C0}^{1-k_2/k_1}(C_{C0} - X_C)^{k_2/k_1}}{k_2/k_1 - k_3/k_1}\right] - \frac{(k_2/k_1)\, C_{C0}^{1-k_3/k_1}}{(1 - k_3/k_1)(k_2/k_1 - k_3/k_1)}(C_{C0} - X_C)^{k_3/k_1} \quad (11)$$

The concentrations of formaldehyde, cardanol, and various methylol cardanols at any time in the mixture are given by the following equation:

$$C_F = C_{F0} - X_F \quad (12)$$

$$C_C = C_{C0} - X_C \quad (13)$$

$$C_M = X_C - X_M \quad (14)$$

$$C_D = X_M - X_D \quad (15)$$

$$C_T = X_D \quad (16)$$

It is evident from eqs. (10) and (11) that X_M and X_D can be calculated for any value of X_C provided that the two ratios of the reaction rate constants k_2/k_1 and k_3/k_1 are known. In an earlier investigation on kinetics of alkaline-catalyzed cardanol–formaldehyde reaction, the two ratios obtained were

$$\frac{k_2}{k_1} = 0.74 \quad \text{and} \quad \frac{k_3}{k_1} = 0.22$$

First of all, the concentration of formaldehyde C_F was determined at different times experimentally by hydroxylamine hydrochloride method. By substitution these values of C_F in eq. (12), the values of X_F were determined. By using eqs. (9)–(11), X_C, X_M, and X_D were calculated for different values of X_F and, finally, for these values of X_C, X_M, and X_D, the concentrations of different species in the mixture, i.e., C_C, C_M, C_D, and C_T were obtained by eqs. (13)–(16).

Product Distribution

In a mixture of 1 mol cardanol and 3 mol formaldehyde, the concentrations of cardanol, monomethylol cardonal, dimethylol cardanol, and trimethylol cardanol at any time, i.e., C_C, C_M, C_D, and C_T, were calculated as mentioned above and plotted[3] against X_F as shown in Figure 1. The composition of the resin could be determined for any degree of completion of the reaction at any stage from this figure.

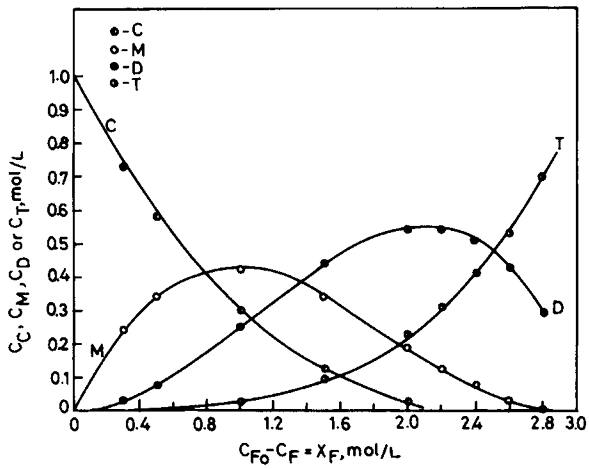

Fig. 1. Product distribution in cardanol–formaldehyde reaction: cardanol (C), monomethyld cardanol (M), dimethylol cardanol (D), trimethylol cardanol (T).

CONCLUSION

For desired properties, the reaction should be immediately stopped by cooling the reaction mixture when the specified composition of resinous product has been achieved. However, it is difficult to analyze all intermediate compounds formed at different stages during the process. By the method suggested, it is possible to get the complete analysis of the product by determining the concentration of only one reactant, viz., formaldehyde in the reaction mixture.

APPENDIX: 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 constant (L/mol · s)
M	monomethylol cardanol
N	normality of NaOH solution used in the neutralization for estimation of formaldehyde
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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