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A Mathematical Model for the Indanylation of m-Cresol with Indene in the Presence of Benzenesulphonic acid

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Abstract

A mathematical model has been developed for the reaction of m-cresol with indene in the presence of benzenesulphonic acid as a catalyst using Yates pattern experimental design and indanyl m-cresol has been obtained in high yield.

Introduction

Friedel Craft's reaction was investigated more than hundred years ago, still the reaction is in the attention of many investigators. This is because of the fact that the products of the reaction have found wide practical utilization in different fields. Among the alkylation processes, alkylation of cresols is very important. To protect synthetic fuels, lubricating oils and polymeric materials against thermal degradation due to heat, light, air, oxygen, ozone etc., use of antioxidant has become increasingly important. Alkyl phenols and their derivatives are excellent antioxidants and multifunctional stabilizers in such media (Babakhanov *et. al.* 1968; Lebedev, 1984; Ravikovich, 1964). Moreover derivatives of alkyl phenols also display herbicidal and bactericidal activities (Melinikov *et. al.* 1954; Nemetkin *et.al.* 1951). Alkylated cresols with long alkyl group are intermediates for surfac tants and detergents (Dritriev *et. al.* 1961). Isomeric cresols have been alkylated with olefins in the presence of different acidic catalysts (Kharchenko and Zavgorodnii, 1964; Saha and Ghosh 1989; Saha and Badruzzaman, 1990; Saha *et. al.* 1998; Saha *et. al.* 2000 and Shulov *et. al.* 1969). But no attempt has so far been made to study the reactions of cresols with indene in the presence of benzenesulphonic acid. Benzenesulphonic acid is milder in its action and does not cause undesirable side reactions (Kurbanov *et. al.* 1978; volfson *et. al.* 1963).

In the present work, the reaction of m-cresol with indene in the presence of benzenesulphonic acid as catalyst has been investigated and a mathematical model for the reaction has been developed.

Materials and Methods

The reactions were carried out in a three necked round bottomed flask fitted with a condenser, a thermometer, a dropping funnel and a stirrer. Mixture of m-cresol (30 g) and benzenesulphonic acid (0.6 - 2.4 g) was charged into the flask, heated to the temperature of the experiment, then indene (8.07 -5.38 g) was introduced into the mixture gradually over a certain period of time (time of addition) with constant stirring. The reaction mixture was stirred for another period of time (time of stirring) at the same temperature after the addition of the total amount of indene. The reaction mass was then cooled to room temperature, dissolved in petroleum ether and neutralized with saturated $NaHCO_3$ solution, then washed with distilled water for several times. Unconverted reactants and solvent were distilled off at atmospheric pressure. The residual product was finally distilled (b.p. 300^{O} C) and the yield was expressed as percentage of theory. Structure of the product was elucidated by spectral means.

Results and Discussion

m-Cresol with indene in the presence of benzenesulphonic acid as catalyst gave indanyl m-cresol.The indanyl group substituted the aromatic ring to the ortho- or para- position with respect to the -OH group. Three parameters viz. temperature, molar ratio of m-cresol to indene and amount of benzenesulphonic acid were considered in the development of the mathematical model of the reaction of m-cresol with indene in the presence of benzenesulphonic acid using Yates pattern experimental design (Clausen 1978).

The experimental ranges of the variables are listed in Table I. The critical response of interest is yield of indanyl m-cresol. Time of addition of indene to m-cresol-catalyst mixture was 2h and time of stirring after the addition of indene was 1 h.

The experimental design used was Yates pattern, 3 factor two level factorial; there were 2^3 i.e. eight trials. Since the basic 2^3 factorial design involved eight trials, each was run in duplicate yielding 16 trials. In order to check

Table I. Process variables and response

Variable	Range		
	Low (-)	Mid (0)	High (+)
X_1 Temperature (^{O}C)	60	100	140
X_2 Molar ratio of m-cresol to indene	4:1	5:1	6:1
X_3 Amount of catalyst, % by wt. of m-cresol	2	5	8

Response: Y - Yield of indanyl m-cresol

the lack of fit due to curvature, additional trial was made at the midpoint level of each factor. The difference between the average centre point value and the overall average of the design points indicated the severity of curvature.

Table II illustrates the two level 3-factor design with the factors in coded form. The experimental runs for trial 1 through 8 were run in duplicate; trial 9, the centre point trial was run four times, interspersed throughout the experimental run.

Table II. Experimental design

Trial No.	Replicates	Design		
		Temperature, X_1	Molar ratio, X_2	Amount of catalyst, X_3
1	2	-	-	-
2	2	+	-	-
3	2	-	+	-
4	2	+	+	-
5	2	-	-	+
6	2	+	-	+
7	2	-	+	+
8	2	+	+	+
9	4	0	0	0

The results of these experiments are listed in the Table III. The average yield $\bar{Y}$, the range- and the variance were calculated for each trial. The variance, which is an estimate of dispersion of data, was calculated by the following formula :

$$\text{variance} = S^2 = \frac{(Y_1 - \bar{Y})^2 + (Y_2 - \bar{Y})^2 + \ldots\ldots + (Y_n - \bar{Y})^2}{n - 1}$$

where, Y = response value, $\bar{Y}$ = average or mean of response values, n = number of observations.

For example, for trial 1,

$$\text{variance} = S_1^2 = \frac{(19.7 - 20.1)^2 + (20.5 - 20.1)^2}{2-1}$$

$$= 0.16+0.16 = 0.32$$

and for trial 9,

$$\text{variance} = S_9^2 = \frac{(46.9 - 47.8)^2 + (48.3 - 47.8)^2 + (47.2 - 47.8)^2 + (48.3 - 47.8)^2}{4-1}$$

$$= 2.42/3 = 0.81$$

The variances calculated for each trial were then used in the calculation of a weighted

average of the individual variances for each trial.

Pooled variance = S^2_{pooled}

$$= \frac{(n_1 - 1)(S_1^2) + (n_2 - 1)(S_2^2) + \ldots + (n_k - 1)(S_k^2)}{(n_1 - 1) + (n_2 - 1) + \ldots\ldots + (n_k - 1)}$$

$$= \frac{1(0.32) + 1(0.72) + 1(0.5) + 1(0.98) + 1(1.28) + 1(1.62) + 1(0.8) + 1(1.62) + 3(0.81)}{1 + 1 + 1 + 1 + 1 + 1 + 1 + 1 + 3}$$

= 0.933

The pooled standard deviation is the square root of the pooled variance:

Standard deviation $_{pooled} = \sqrt{S^2_{pooled}} = 0.966$

The pooled standard deviation was used to calculate the minimum observed effect that was statistically significant.

The computation analysis for this experiment is shown in the Table IV. The design matrix was supplemented with a computation matrix, which was used to detect any interaction effects. This computation matrix was generated by simple algebraic multiplication of the coded factor levels. In trial 1, X_1 was minus, X_2 was minus, therefore, X_1X_2 was plus; in trial 2, X_1 was plus, X_2 was minus, therefore X_1X_2 was minus. The column at the far right of the table is the average yield for each trial. The sum +'s row was generated by totaling the response values on each row with a plus for each column. For X_1 factor, 40.8 + 45.8 + 56.0 + 74.2 = 216.8. In the similar manner the sum -'s row was generated. The sum of these two rows should equal the sum of all the average responses and was included as a check on the calculations. The differ

Table III. Results of three-factor experiment

Trial No.	Results				
	Yield %			Range	Variances
	Y_1	Y_2	$\bar{Y}$		
1	19.7	20.5	20.1	1	0.32
2	40.2	41.4	40.8	1	0.72
3	37.2	38.2	37.7	1	0.50
4	45.1	46.5	45.8	1	0.98
5	49.1	50.7	49.9	2	1.28
6	55.1	56.9	56.0	2	1.62
7	66.4	66.0	66.2	2	0.80
8	73.3	75.1	74.2	2	1.62
9	46.9 47.2	48.3 48.8	47.8	2	0.81

Table IV. Computation matrix for three factor experiment

Trial	Mean	Design			Computation				Response
		X_1	X_2	X_3	X_1X_2	X_1X_3	X_2X_3	$X_1X_2X_3$	$\overline{Y}$
1	+	-	-	-	+	+	+	-	20.1
2	+	+	-	-	-	-	+	+	40.8
3	+	-	+	-	-	+	-	+	37.7
4	+	+	+	-	+	-	-	-	45.8
5	+	-	-	+	+	-	-	+	49.9
6	+	+	-	+	-	+	-	-	56.0
7	+	-	+	+	-	-	+	-	66.2
8	+	+	+	+	+	+	+	+	74.2
Sum +'s	390.7	216.8	223.9	246.3	190.0	188.0	201.3	202.6	
Sum -'s	0	173.9	166.8	144.4	200.7	202.7	189.4	188.1	
Sum	390.7	390.7	390.7	390.7	390.7	390.7	390.7	390.7	
Difference	390.7	42.9	57.1	101.9	-10.7	-14.7	11.9	14.5	
Effect	48.83	10.73*	14.28*	25.48*	-2.68*	-3.68*	2.98*	3.63*	

Curvature = 48.83 - 47.80 = 1.03

ence row represented the difference between the responses in the four trials when the factor was at a high level and the responses in the four trials when the factor was at a low level. The effect was then calculated by dividing the difference by the number of plus signs in the column. In the first column, labeled mean, the effect row value is the mean or average of all data points. The average of the centre point runs, Trial 9, was then subtracted from the mean effect to give a measure of curvature.

The minimum significant factor effect [MIN] and the minimum significant curvature effect [MINC] were again derived from t-test significance criteria. The relationships are:

$$[\text{MIN}] = t.s\sqrt{\frac{2}{m.k}}$$

$$[\text{MINC}] = t.s\sqrt{\frac{1}{m.k}+\frac{1}{c}}$$

where, t = appropriate value from "t table", s = pooled standard deviation, m = number of plus signs in column, k = number of replicates in each trial, c = number of centre points.

The t value of 2.20 was from the students' "t" table for the 95 % confidence level and 11 degrees of freedom (Davies 1979). The degrees of freedom resulted from eight trials with two replicates and one trial with four replicates.

Degrees of freedom = 8(2 - 1) + 1(4 - 1) = 11

The calculation for the minimum significant effects was as follows :

$$[MIN] = 2.20 \times 0.966 \sqrt{\frac{2}{4x2}} = 1.06$$

$$[MINC] = 2.20 \times 0.966 \sqrt{\frac{1}{8x2} + \frac{1}{4}} = 1.188$$

Applying these criteria to the calculated effects, it was seen that the effects of temperature (X_1), molar ratio of *m*-cresol to indene (X_2), amount of benzenesulphonic acid (X_3), interactions between temperature and amount of benzenesulphonic acid (X_1X_3), molar ratio of m-cresol to indene and amount of benzenesulphonic acid (X_2X_3), temperature and molar ratio of *m*-cresol to indene (X_1X_2) and among temperature, molar ratio of *m*-cresol to indene and amount of benzenesulphonic acid ($X_1X_2X_3$) were significant. There was no significant curvature effect. These results were expressed as a mathematical model using a first order polynomial. The values for the co-efficients were one half the factor effects listed in the Table. Since these were based upon coded levels +1 and -1 that differed by two units.

$$Y = 48.83 + 5.365X_1 + 7.14X_2 + 12.74X_3 - 1.34X_1X_2 - 1.84X_1X_3 + 1.49X_2X_3 + 1.815X_1X_2X_3$$

In this equation the factors were expressed in coded units. These were converted into real units by substituting:

for temperature T(^{O}C), X_1

$$= \frac{T - (140 + 60)/2}{(140 - 60)/2} = \frac{T - 100}{40}$$

for molar ratio(m:1), X_2

$$= \frac{m - (6 + 4)/2}{(6 - 4)/2} = m - 5$$

for the amount of catalyst (y), X_3

$$= \frac{y - (8+2)/2}{(8-2)/2} = \frac{y - 5}{3}$$

This substitution yielded the following final expression :

$$Y = 48.83 + 5.365 \times \frac{T-100}{40} + 7.14 \times (m-5) + 12.74 \times \frac{y-5}{3} - 1.34 \times \frac{T-100}{40} \times (m-5) - 1.84 \times \frac{T-100}{40} \times \frac{y-5}{3} + 1.49 \times (m-5) \times \frac{y-5}{3} + 1.815 \times \frac{T-100}{40} \times (m-5) \times \frac{y-5}{3}$$

$$Y = -71.33 + 0.756T + 15.57m + 10.86y - 0.11Tm - 0.091Ty - 1.015my + 0.015Tmy$$

For trial 1, temperature(T) = 60^{O} C, molar ratio of m-cresol to indene (m:1) = 4:1, and the amount of catalyst (y) = 2 % by wt. of *m*-cresol.

Therefore, yield calculated from the derived model,

$$Y_{(calc)} = -71.33 + 0.756\acute{}60 + 15.57\acute{}4 + 10.86\acute{}2 - 0.11\acute{}60\acute{}4 - 0.091\acute{}60\acute{}2 - 1.015\acute{}4\acute{}2 + 0.015\acute{}60\acute{}4\acute{}2 = 19.79$$

Experimental average yield of the trial 1, $Y_{(exp.)}$ = 20.1

Deviation =0.31. Percentage deviation = 1.54

All the values of the experimental average yield and the calculated yield from the derived equation are shown in the Table V.

Table V. Experimental average yield and calculated yield

Trial	$Y_{(exp.)}$	$Y_{(calc.)}$	Deviation	Percentage deviation
1	20.1	19.79	0.31	1.54
2	40.8	40.11	0.69	1.69
3	37.7	37.27	0.43	1.14
4	45.8	44.79	1.01	2.21
5	49.9	49.43	0.47	0.94
6	56.0	54.87	1.13	2.02
7	66.2	65.53	0.67	1.01
8	74.2	72.57	1.63	2.19

The discrepancies between the experimental and calculated values did not exceed 2.21 %.

Table VI. The ^{1}H NMR -spectrum of indanyl *m*-cresol

Observed signals of the protons	Chemical shift in δ ppm
Aromatic ring protons	6.95-7.33
-OH group proton	6.62-6.80
All the protons on the indanyl group except four on aromatic ring	3.08-3.56
Three protons on the -CH_3 group	2.39

In the UV-spectrum, the product absorbed strongly at λ_{max}= 293.5 nm in 0.01M methanol solution.

IR-spectrum showed absorption band at 3390-3400cm^{-1} for the presence of -OH group. Band at 740-760 cm^{-1} showed the presence of 1,2,3-trisubstituted benzene ring.

Bands near 810 and 860 cm^{-1} accounted for 1,2,4-trisubstituted benzene ring and at 2910 cm^{-1} for the saturated C-H stretch.

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