STUDIES IN DEALKYLATION—DEVELOPMENT OF A REACTION RATE MODEL

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ABSTRACT

A reaction rate model was proposed for the dealkylation of isomers of xylene and ethylbenzene based on the model building techniques and the model was tested using the calculated parametric values.

Dealkylation of the isomers of xylene and ethylbenzene was studied with the initial concentration of hydrocarbon, initial concentration of hydrogen and reaction temperature as the three variables in the factorial design of experiments. At each of these design points data were obtained which formed the basis for the initial estimates for further calculations. An iterative procedure was followed to obtain the final values of the parameters. From these values, the activation energy and frequency factor for each system were estimated. These were found to be in good agreement with the reported values, thereby establishing the validity of the rate model.

Key words: Dealkylation; Reaction Rate Model.

INTRODUCTION

Box and Hunter [1], Hunter and Mazaki [2] describe a simple method for iterative model building techniques in which statistical analysis is applied to the estimated parameters of a theoretical reaction rate model rather than to the original observations themselves. In the model building technique one can build a model either for the order of the reaction or for the mechanism of the reaction. In the present investigation an attempt is made to propose a model for the dealkylation of isomers of xylene and ethylbenzene.

Present systems

Vapour phase hydrodealkylation of alkyl aromatic hydrocarbons was investigated over nickel on silica gel catalyst. The reactants studied in detail

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were m-xylene, o-xylene and ethyl benzene. The reactions can be written as :

$$C_6H_4(CH_3)_2 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \tag{1}$$

$$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4 \tag{2}$$

ethylbenzene

$$C_6H_5C_2H_5 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \tag{3}$$

$$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4 \tag{4}$$

Ravindram [3], and Weiss and Doelp [4] have carried out reaction rate studies and reported that the orders of the above reactions are first order with respect to the hydrocarbon and half order with respect to hydrogen. For xylene or ethylbenzene depletion, the rate can be written in terms of the mole fractions as :

$$-\frac{d(n_x)}{d(W/F)} = k_1 n_x n_H^{0.5} \tag{5}$$

for toluene depletion,

$$\frac{d(n_T)}{d(W/F)} = k_1 n_x n_H^{0.5} - k_2 n_T n_H^{0.5} \tag{6}$$

and for benzene formation,

$$\frac{d(n_B)}{d(W/F)} = k_2 n_T n_H^{0.5} \tag{7}$$

EXPERIMENTAL

The apparatus mainly consists of feeding devices for hydrocarbon and hydrogen, preheaters for the reactants, reactor proper and product collecting unit. A previous paper [5] describes the experimental set up, catalyst preparation, operating procedure and other details.

Experimental Designs

Three variables—initial concentration of the hydrocarbon, initial concentration of hydrogen and reaction temperature were taken as the three factors and a 2^3 factorial design was built for the model building experiments. The complete design with the coded levels and the actual values of the input variables is presented in Table I. At each of these eight design points runs were conducted to establish the relation between the time factor (W/F) and conversion. Representative plots are presented in Figs. 1, 2 and 3. Tables II, III and IV present the data in terms of the mole fraction of each component. For analysis of the model, only toluene rate has been taken into consideration. However, the mole fractions of xylene or ethylbenzene and hydrogen were taken in the rate equation by using the Lagrange's interpolation formula. From these plots the initial estimates of the parameters were evaluated. Using these initial estimates of the parameters, the true estimates of the parameters were evaluated by the method of iteration using a Elliot 803 computer. The final estimates of the parameters were taken for the case when the residual sum of squares is minimum. The true estimates of the parameters are presented in Table V. These estimates of the parameters are taken as the response and factorial analysis was performed. The results of the factorial analysis are presented in Table VI. A sample calculation for the above method is given for m-xylene. For evaluation of k_1 and k_2 the results obtained for one set of conditions are presented below :

Conditions : Treatment — + —
Initial concentration of m-xylene : 0·07142
Initial concentration of hydrogen : 0·58714
Reaction temperature: 500° C

W/F	% conversion Benzene	% conversion Toluene	Total conversion
15	..	5·95	5·95
17	..	7·2	7·2
20	0·8	8·3	9·1
25	0·9	8·6	9·5
30	2·2	11·1	13·3

For finding out k_1 and k_2, the W/F Vs conversion data can be differentiated and rate data thus obtained can be used to evaluate the specific reaction rate constants by the method of least squares. This, however, involves the differentiation of the integral rate data. An alternative method has been employed. Taking equation (6) into consideration the equation can be integrated numerically and the solution for a particular point can be notionally written as:

$$x_{T1} = k_1 x_1 - k_2 Y_1 \tag{8}$$

TABLE I

Variable	Coded name	Coded level	
		—1	+1
Initial concentration of hydrocarbon	A	0·07142	0·14285
Initial concentration of hydrogen	B	0·42852	0·85710
Temperature	C	500	550

We have five data points and at each point the equation can be integrated taking the actual observed points, or in general, equation (8) can be written as:

$$n_{Ti} = k_1 X_i - k_2 Y_i \tag{9}$$

As there are five equations and two unknowns, the best values of these were obtained assuming k_1 and k_2 values and verifying how they agree with the experimental data. The agreement between the calculated and experimental values was expressed as the residual sum of squares:

$$\text{R.M.S.} = \sum_{i=1}^{N} (n_{Ti}\,\text{cal} - n_{Ti}\ Obs)^2 \tag{10}$$

where N is the number of data points.

The values of k_1 and k_2 were varied in such a way that a minimum value of the residual sum of squares resulted. These values of k_1 and k_2 were taken as the best estimates.

To start the iterative procedure some initial values of k_1 and k_2 are needed. These values were calculated from conversion Vs W/F and Equations (5) and (6).

Taking Equation (5)

at $t = 0$ $\qquad n_x = n_{xc}$

$$n_H = n_{HC}$$

$$k_1 = \frac{\text{Initial slope}}{n_{x0} \times n_{HQ}{}^{0.5}}$$

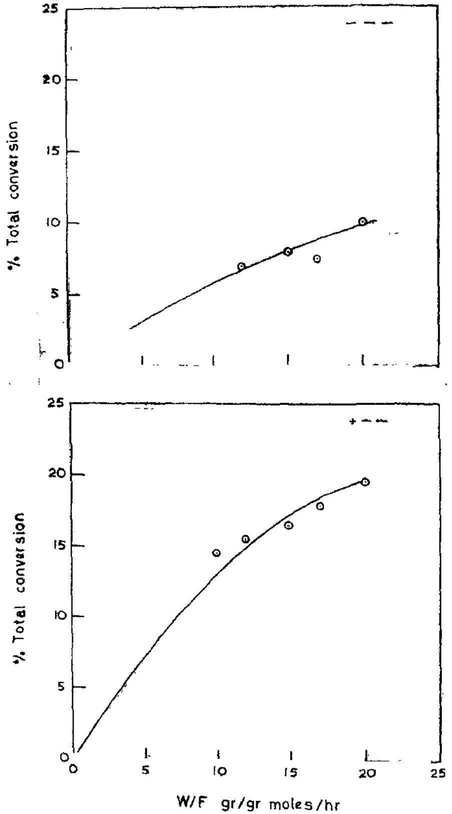

FIG. 1. Effect of W/F on total conversion at each design point (*m*-Xylene).

Here $n_{xc} = 0\cdot07142$

$n_{HC} = 0\cdot58714$

nad Initial slope $= 0\cdot4196 \times 10^{-3}$

$k_1 = 0\cdot6347 \times 10^{-2}$

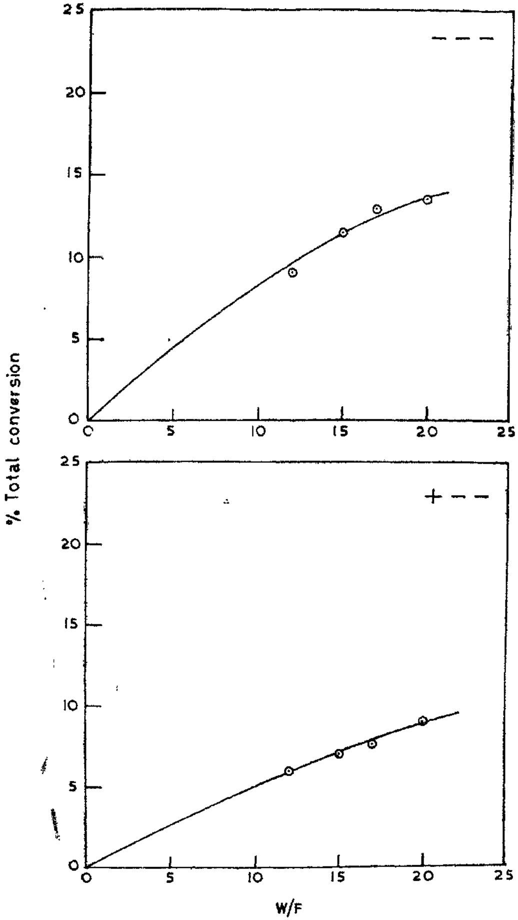

FIG. 2. Effect of W/F on total conversion at each of the design point (*o*-Xylene).

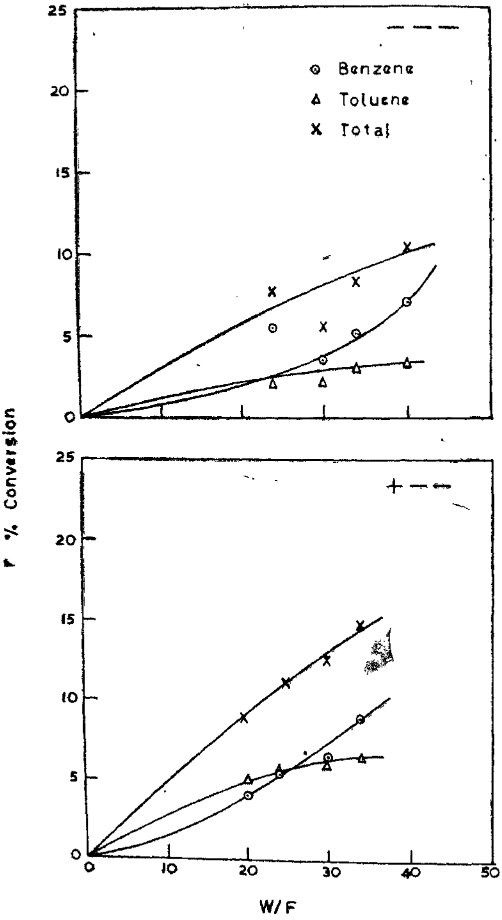

FIG. 3. Effect of W/F at each of the design point (Ethyl Benzene).

TABLE II

Effect of time factor (W/F) on m-*xylene conversion at each of the design points*

t (W/F)	n_T (mole fraction of toluene) × 10^3	n_X (mole fraction of m-xylene) × 10^2	n_H (mole fraction of hydrogen) × 10^2
Treatment — — —			
0	0	7·14	42·86
12	4·79	6·62	39·73
15	5·71	6·43	38·57
17	5·14	6·63	39·77
20	7·21	6·36	38·18
Treatment + — —			
0	0	14·29	42·86
10	16·57	12·29	36·86
12	21·71	12·11	36·34
15	24·00	11·89	35·66
17	25·86	11·70	35·70
20	27·57	11·53	34·59
Treatment — + —			
0	0	7·14	85·71
15	4·25	6·72	80·61
17	5·14	6·63	79·54
20	5·93	6·49	77·91
25	6·14	6·47	77·61
30	7·93	6·19	74·31
Treatment + + —			
0	0	14·29	85·71
15	8·71	13·41	80·49
17	9·71	13·31	79·89
20	10·99	13·19	79·11
25	11·29	13·16	78·94
30	12·43	12·99	77·61
Treatment — — +			
0	0	7·14	42·86
12	7·86	6·34	38·01
15	9·36	6·17	37·03
17	10·99	5·96	35·55
20	15·71	5·52	33·12
Treatment + — +			
0	0	14·29	42·86
10	6·14	13·67	41·02
12	11·43	13·14	39·43
15	8·86	13·40	40·20
17	36·28	10·51	31·54
20	0·71	12·61	37·24

TABLE II (*Contd.*)

t	$n_T \times 10^3$	$n_X \times 10^2$	$n_H \times 10^2$
	Treatment $-++$		
0	0	7·14	85·71
15	14·43	5·61	67·37
17	17·57	5·21	62·57
20	19·14	5·08	60·94
25	20·86	4·88	58·54
	Treatment $+++$		
0	0	14·29	85·71
15	20·86	11·98	71·83
17	26·57	11·26	67·59
20	33·71	10·43	62·57
25	31·71	10·63	63·81
30	39·43	9·64	57·82

From Equation (6)

at $t = t_{\max}$ (t at $n_T = n_{T\max}$)

$$\frac{d(n_T)}{dt} = 0$$

$$\frac{k_1}{k_2} = \frac{n_{T\max}}{n_x\,(\text{at } n_T)_{\max}}$$

$$k_2 = 0 \cdot 066824.$$

So taking these values of k_1 and k_2 the iterative procedure was performed with an increment of 0·001 to the values of the k_1 and k_2 and finding out the minimum deviation and from this, the new values of k_1 and k_2 for second

TABLE III

Effect of time factor (W/F) on o-xylene conversion at each of the design points

t (W/F)	n_T (mole fraction of toluene) × 10^3	n_X (mole fraction of o-xylene) × 10^2	n_H (mole fraction of hydrogen) × 10^2
	Treatment — — —		
0	0	7·14	42·86
12	4·99	6·49	38·96
15	5·71	6·32	37·93
17	6·43	6·21	37·29
20	5·21	6·18	37·07
	Treatment + — —		
0	0	14·29	42·86
12	7·29	13·41	40·24
15	8·57	13·27	39·81
17	9·99	13·20	39·60
20	9·99	12·99	38·96
	Treatment — + —		
0	0	7·14	85·71
17	4·93	6·50	78·00
20	5·93	6·37	76·46
25	6·29	6·25	75·00
30	8·21	6·09	73·03
	Treatment + + —		
0	0	14·29	85·71
17	11·43	12·86	77·14
20	12·71	12·64	75·86
25	14·29	12·36	74·14
30	16·71	12·07	72·43
	Treatment — — +		
0	0	7·14	42·86
12	4·43	6·28	39·77
15	5·36	6·50	39·00
17	5.43	6·45	38·70
20	5·79	6·36	38·14
	Treatment + — +		
0	0	14·29	42·86
10	6·71	13·36	40·07
12	7·57	13·21	39·64
15	9·71	13·00	39·00
17	10·42	1 ·86	38·57
20	111·42	12·64	37·93

TABLE III (*Contd.*)

t	$n_T \times 10^3$	$n_X \times 10^2$	$n_H \times 10^2$
	Treatment $- + +$		
0	0	7·14	85·71
17	2·86	6·82	81·86
20	3·57	6·75	81·00
25	4·29	6·64	79·71
30	4·50	6·61	79·29
	Treatment $+ + +$		
0	0	14·29	85·71
15	7·86	13·21	79·29
17	8·57	13·13	78·77
20	8·71	13·00	78·00
25	10·29	12·86	77·14
30	11·43	12·70	76·20

iteration. To find out the corrected values of k_1 and k_2 the following procedure was followed:

D_1 = mean square deviation for the 1st, 3rd and 5th levels.

D_2 = mean square deviation for the 2nd and 4th levels.

and P_1 and P_2 are the correction for the second iteration.

k_{10}, k_{20} are the initial values for the first iteration.

Then the criteria for the minimum deviation is

$$D(k_{10} + P_1,\ k_{20} + P_2) = D(k_{10},\ k_{20}) + P_1 \frac{\delta D}{\delta k_{10}} + P_2 \frac{\delta D}{\delta k_{20}} = 0 \quad (11)$$

We have two sets of equations,

$$D_1(k_{10},\ k_{20}) + P_1 \frac{\delta D_1}{\delta k_{10}} + P_2 \frac{\delta D_1}{\delta k_{20}} = 0 \quad (12)$$

$$D_2(k_{10},\ k_{20}) + P_1 \frac{\delta D_2}{\delta k_{10}} + P_2 \frac{\delta D_2}{\delta k_{20}} = 0 \quad (13)$$

$\frac{\delta D_1}{\delta k_{10}}, \frac{\delta D_1}{\delta k_{20}}, \frac{\delta D_2}{\delta k_{10}}, \frac{\delta D_2}{\delta k_{20}}$ were found by actually giving increments

TABLE IV

Effect of time factor (W/F) on ethylbenzene conversion at each of the design points

t (W/F)	n_T (mole fraction of toluene) × 10^3	n_X (mole fraction of ethylbenzene) × 10^2	n_H (mole fraction of hydrogen) × 10^2
Treatment − − −			
0	0	7·14	42·86
24	1·64	6·74	40·41
30	1·71	6·71	40·29
34	2·25	6·50	39·00
40	2·50	6·39	38·34
Treatment + − −			
0	0	14·29	42·86
20	7·57	12·98	38·94
24	8·21	12·71	38·14
30	7·71	12·69	38·08
34	8·21	12·17	36·51
Treatment − + −			
0	0	7·14	85·71
34	6·89	6·28	75·34
40	7·14	6·15	75·09
50	8·04	5·79	69·51
60	10·86	4·94	59·31
Treatment + + −			
0	0	14·29	85·71
34	22·00	11·88	71·21
40	22·14	11·01	66·06
50	22·57	11·00	66·00
60	30·86	9·33	55·97
Treatment − − +			
0	0	7·14	42·86
24	4·08	6·39	38·31
30	4·43	6·16	36·99
34	5·04	5·98	35·87
40	6·29	5·24	31·44
Treatment + − +			
0	0	14·29	42·86
20	4·29	13·03	39·09
24	4·64	13·12	39·36
30	7·00	12·70	38·10
34	6·00	12·76	38·27

TABLE IV (*Contd.*)

t	$n_T \times 10^3$	$n_E \times 10^2$	$n_H \times 10^2$
	Treatment $-++$		
0	0	7·14	85·71
34	6·96	5·54	66·43
40	8·11	5·26	63·13
50	10·53	4·72	56·61
60	12·64	4·28	42·77
	Treatment $+++$		
0	0	14·29	85·71
34	22·00	11·07	66·43
40	27·86	8·51	63·13
50	28·28	7·79	56·61
60	38·86	6·19	50·49

to k_{10} and k_{20}. Equations (12) and (13) were solved to find P_1 and P_2. New values of k_1 and k_2 for the next iteration were taken as

$$k_{11} = k_{10} + P_1$$

$$k_{21} = k_{20} + P_2$$

After the seventh iteration the results are given as,

$k_1 = 0\cdot46123 \times 10^{-2}$ $\quad$ $k_2 = 0\cdot1 \times 10^{-4}$

n_T (cal)	n_T (obs)
$0\cdot376490 \times 10^{-2}$	$0\cdot424949 \times 10^{-2}$
$0\cdot43159 \times 10^{-2}$	$0\cdot514224 \times 10^{-2}$
$0\cdot512047 \times 10^{-2}$	$0\cdot592766 \times 10^{-2}$
$0\cdot633123 \times 10^{-2}$	$0\cdot614212 \times 10^{-2}$
$0\cdot772925 \times 10^{-2}$	$0\cdot792762 \times 10^{-2}$

Residual sum of squares : $0\cdot3459103 \times 10^{-6}$

After this iteration the residual sum of squares increased and so these values of k_1 and k_2 were taken as the best estimates of k_1 and k_2.

TABLE V

The rate constants in the model

Treatment	*m*-xylene $k_1 \times 10^3$	*m*-xylene $k_2 \times 10^3$	*o*-xylene $k_1 \times 10^3$	*o*-xylene $k_2 \times 10^3$	ethylbenzene $k_1 \times 10^3$	ethylbenzene $k_2 \times 10^3$
$---$	15·48	81·03	99·76	15·65	1·64	3·76
$+--$	0·01	0·01	11·20	147·90	3·16	7·58
$-+-$	4·61	0·01	8·46	845·00	4·91	0·01
$++-$	0·01	0·01	0·01	0·15	0·01	0·01
$--+$	4·38	174·30	647·94	166·35	1·36	0·01
$+-+$	74·83	0·01	1·68	220·00	1·52	68·08
$-++$	11·98	897·00	5·39	1180·32	5·40	2·85
$+++$	7·77	0·01	88·11	22·43	89·00	23·55

The standard deviation for the above calculations was found using the general equation

$$\sigma = \sqrt{\Sigma d/N - 1}$$

where $d = \%$ deviation $= \dfrac{n_T\,(\text{expt}) - n_T\,(\text{cal})}{n_T\,(\text{expt})} \times 100$

and $N =$ number of data points.

$\sigma = 11{\cdot}22\%$

Analysis of the constants

The temperature dependance of the rate constants can be given by Arrhenius' law as

$$k_1 = \alpha_1\, e^{-\beta_1/T} \tag{14}$$

$$k_2 = \alpha_2\, e^{-\beta_2/T} \tag{15}$$

where α_1 and α_2 are the frequency factors and β_1 and β_2 are constants.

TABLE VI

Factional analysis on $\ln k_1$ *and* $\ln k_2$

Effect	*m*-xylene $10 \ln k_1$	 $10 \ln k_2$	*o*-xylene $10 \ln k_1$	 $10 \ln k_2$	ethylbenzene $10 \ln k_1$	 $10 \ln k_2$
A	−19·85	−37·71	−12·23	−14·45	− 9·99	9·54
B	− 3·08	− 9·20	−10·02	− 5·08	0·72	− 8·29
C	19·08	15·21	13·64	11·99	10·05	6·84
AB	− 3·93	9·20	2·24	−20·76	−11·96	−23·49
AC	13·84	15·21	4·33	14·99	3·81	− 7·04
BC	− 0·08	13·30	7·94	2·15	12·37	5·79
ABC	− 4·24	−13·30	19·50	6·41	11·97	− 6·84
Mean	−62·35	−77·41	−49·84	−25·59	−62·44	−94·22

Taking natural logarithms of both sides of Equations (14) and (15) we get

$$\ln k_1 = \ln \alpha_1 - \beta_{1/T} \tag{16}$$

$$\ln k_2 = \ln \alpha_2 - \beta_{2/T} \tag{17}$$

Defining the average log rate constant as

$$\ln ki = \ln \alpha_i - \beta_i \bar{T}^{-1} \, (i = 1,\ 2) \tag{18}$$

On subtracting (18) from (16) and (17) we get

$$\ln k_1 = \ln k_1 - \beta_1 \, (T^{-1} - \bar{T}^{-1}) \tag{19}$$

$$\ln k_2 = \ln k_2 - \beta_2 \, (T^{-1} - \bar{T}^{-1}) \tag{20}$$

The estimates of the unknown are provided by

$$\beta_1 = \frac{C_i \text{ effect}}{\frac{1}{T^-} - \frac{1}{T^+}} \, (i = 1,\ 2) \tag{21}$$

TABLE VII

	Activation Energy E_1	E_2	Frequency factor α_1	α_2
m-xylene	49·044	39·105	$1{\cdot}148 \times 10,^{3}$	$2{\cdot}630 \times 10^{10}$
o-xylene	35·075	30·828	$2{\cdot}203 \times 10^{9}$	$1{\cdot}629 \times 10^{8}$
ethylbenzene	25·930	17·610	$4{\cdot}266 \times 10^{13}$	$1{\cdot}774 \times 10^{9}$

where 'C_1 effect' refers to the C effect calculated from $ln\ k_1$ and 'C_2 effect' hat calculated from $ln\ k_2$.

The activation energy of the reaction is given by

$$E = R\beta$$

vhere R is the gas constant. The activation energies and the frequency actors for each system are presented in Table VII. The values agree with he values given by Weiss and Doelp (1964).

The rate equations for the systems investigated can now be written as m-xylene :

$$-\frac{d\,(n_x)}{d\,(W/F)} = 1{\cdot}148 \times 10^{13}\ e^{-49,\,044/RT}\, n_x\, n_H{}^{0\cdot5}$$

$$\frac{d\,(n_T)}{d\,(W/F)} = 1{\cdot}148 \times 10^{13}\ e^{-49,\,014/RT}\, n_x\, n_H{}^{0\cdot5}$$

$$-\,2{\cdot}63 \times 10^{10}\ e^{-39,\,105\cdot RT}\, n_T\, n_H{}^{0\cdot5}\ .$$

o-xylene :

$$-\frac{d\,(n_x)}{d\,W/F)} = 2{\cdot}208 \times 10^{9}\ e^{-35,\ 075/RT}\, n_x\, n_H{}^{0\cdot5}$$

$$\frac{d\,(n_T)}{d\,(W/F)} = 2{\cdot}208 \times 10^{9}\ e^{-35,\,075/RT}\, n_x\, n_H{}^{0\cdot5}$$

$$-\,1{\cdot}629 \times 10^{8}\, e^{-30,\,828/RT}\, n_T\, n_H{}^{0\cdot5}$$

ethylbenzene :

$$-\frac{d(n_E)}{d(W/F)} = 4\cdot266 \times 10^{13}\ e^{-25,930/RT}\, n_E\, {n_H}^{0\cdot5}$$

$$\frac{d(n_T)}{d(W/F)} = 4\cdot266 \times 10^{13}\ e^{-25,930/RT}\, n_E\, {n_H}^{0\cdot5}$$

$$-\ 1\cdot774 \times 10^{9}\ e^{-17,810/RT}\, n_T\, {n_H}^{0\cdot5}$$

NOMENCLATURE

D : Square mean deviation
E : Activation energy
F : Flow rate of the feed
k : Reaction rate constant
n : Mole fraction of component
P : Increment in iteration
R : Gas constant
r : Reaction rate
T : Temperature
t : Time factor (W/F)
W : Weight of the catalyst
X : Factor in iteration equation
Y : Factor in iteration equation
σ : Standard deviation
α : Frequency factor
β : Constant

SUBSCRIPTS

B : Benzene
H : Hydrogen
T : Toluene
X : Xylene

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