The Kinetics of the Catalytic Isomerization and Transalkylation of Cumene

D. A. BEST AND B. W. WOJCIECHOWSKI

Department of Chemical Engineering, Queen's University, Kingston, Canada K7L 3N6

The activation energies of three transalkylation reactions which accompany the cracking of cumene on LaY have been measured. Consideration of the magnitudes of these activation energies and of the associated frequency factors leads us to conclude that these are reactions which proceed by a concerted mechanism and that the addition of a methyl group to the aromatic ring is favored over addition to the isopropyl group of cumene. Disproportionation of two cumenes to benzene and diisopropyl benzene tends to favor unexpectedly the formation of the *meta* isomer at ~500°C. However, inspection of the rate parameters shows that, at room temperature, the formation of the *para* isomer will be favored, in keeping with conventional wisdom in such matters. The isomerization of cumene to *n*-propyl benzene appears to involve an almost complete bond separation in the transition state and constitutes the only observed monomolecular primary side reaction accompanying the cracking of cumene.

INTRODUCTION

In previous publications (*1*, *4*) we have shown that the selectivity behavior of a complex reaction on an aging catalyst can be characterized by a family of cat/oil loops, the morphology of which depends on the aging characteristics of the catalyst. This system of loops can in turn be enveloped by a single curve called the Optimum Performance Envelope (OPE). Now, the OPE represents the selectivity behavior of the system in the absence of decay (*1*). Thus, having determined the OPEs one can proceed to use analytical techniques which normally apply to kinetic data obtained in nonaging systems.

DEDUCING THE KINETICS OF MINOR PRODUCT FORMATION FROM INITIAL SELECTIVITIES

The rate constants for the initial rate of formation of primary reaction products on an aging catalyst can be determined using initial selectivities of the Optimum Performance Envelopes and the absolute rate of any one of the primary reactions. To illustrate this it is convenient to refer once again to the Delta mechanism for cumene dealkylation developed in Ref. (*3*) and shown in Fig. 1.

According to this mechanism, if only cumene (C), benzene (Z), and propylene (Y) are present in the reaction mixture, the rate of disappearance of cumene $(-r_c)$ is written as

$$-r_c = k_2{}^*[CS] - k_{-2}{}^*[YS][Z], \quad (1)$$

where $[YS]$ and $[CS]$ represent, respectively, the concentrations of absorbed propylene and cumene.

Substituting for $[CS]$ and $[YS]$ in terms of the appropriate Langmuir adsorption isotherms and accounting for catalyst

243

aging leads to

$$-r_c = \frac{k_2 K_1[\mathrm{C}][\mathrm{S_0}](1 + Gt)^{-1} - k_{-2} K_3[\mathrm{Y}][\mathrm{Z}][\mathrm{S_0}](1 + Gt)^{-1}}{1 + K_1[\mathrm{C}] + K_3[\mathrm{Y}] + K_4[\mathrm{Z}]}, \quad (2)$$

which reduces at zero catalyst age and at conversions approaching zero to

$$-r_{c1} = \left. \frac{k_2 K_1[\mathrm{S_0}][\mathrm{C_0}]}{1 + K_1[\mathrm{C_0}]} \right\} \quad \begin{array}{l} [\mathrm{C}] \to [\mathrm{C_0}] \\ t \to 0 \end{array}. \quad (3)$$

In these expressions, k_2 represents the rate constant for the dealkylation reaction; K_1, K_3, and K_4 represent the adsorption equilibrium constants for cumene, propylene, and benzene; and $[\mathrm{S_0}]$ represents the concentration of active sites at $t = 0$. Complete details of the development of Eq. (1) are given elsewhere (2).

It is apparent from previous work (1) that cumene can also react to products other than benzene and propylene. If it reacts in a monomolecular fashion, as in the case of the formation of n-propyl benzene, then an expression analogous to Eq. (3) is obtained for the rate of loss of cumene to product A:

$$-r_{c2} = k_{\mathrm{A}} \left. \frac{K_1[\mathrm{S_0}][\mathrm{C_0}]}{1 + K_1[\mathrm{C_0}]} \right\} \quad \begin{array}{l} [\mathrm{C}] \to [\mathrm{C_0}] \\ t \to 0 \end{array}. \quad (4)$$

If the loss of cumene occurs in a bimolecular fashion according to a Rideal mechanism, then the rate of reaction of cumene to that
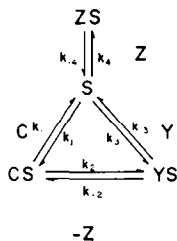

Fig. 1. The Delta mechanism for the dealkylation of cumene. C, Cumene; S, active site; Y and Z, the reaction products. CS, YS, and ZS represent the corresponding adsorbed species.

particular product would be

$$-r_{c3} = k_{\mathrm{B}} \frac{K_1[\mathrm{S_0}][\mathrm{C_0}]^2}{1 + K_1[\mathrm{C_0}]}. \quad (5)$$

Finally, if the bimolecular reaction were of the Hinshelwood type, then

$$-r_{c4} = k_{\mathrm{D}} \left(\frac{K_1[\mathrm{S_0}][\mathrm{C_0}]}{1 + K_1[\mathrm{C_0}]} \right)^2. \quad (6)$$

Taking into account all these possibilities, the overall rate of loss of cumene can be written as

$$\Sigma - r_{ci} = -r_c = \left(\frac{K_1[\mathrm{S_0}][\mathrm{C_0}]}{1 + K_1[\mathrm{C_0}]} \right)$$
$$\times (\sum_{i=1}^{n} k_i + [\mathrm{C_0}] \sum_{j=1}^{m} k_j)$$
$$+ \left(\frac{K_1[\mathrm{S_0}][\mathrm{C_0}]}{1 + K_1[\mathrm{C_0}]} \right)^2 (\sum_{h=1}^{l} k_h). \quad (7)$$

From consideration of the various mechanisms for product formation (1) it appears that the bimolecular reactions resulting in ethyl benzene, cymene, p- and m-diisopropyl benzene, butene, and isobutene occur by Rideal mechanisms. In that case the initial overall rate of loss of cumene at zero catalyst age can be simplified somewhat to

$$-r_c = \left(\frac{K_1[\mathrm{S_0}][\mathrm{C_0}]}{1 + K_1[\mathrm{C_0}]} \right)$$
$$\times (\sum_{i=1}^{n} k_i + [\mathrm{C_0}] \sum_{j=1}^{m} k_j). \quad (8)$$

We now examine the relative rate of formation of the various reaction products. A procedure such as that carried out above

will produce the following expression for the rate of formation of an arbitrary product "A"

$$r_A = k_A \frac{K_1[S_0][C_0]^n}{1 + K_1[C_0]}, \qquad (9)$$

where k_A is the rate constant for the formation of A, and n is the order of the reaction with respect to cumene. The ratio of Eqs. (8) and (9) is quite clearly the initial selectivity for A which can be obtained from the slope of the OPE for component A at zero conversion of cumene:

$$\begin{pmatrix} \text{Initial slope of the OPE} \\ \text{for product A} \end{pmatrix}$$
$$= \frac{r_A}{-r_c} = \frac{k_A[S_0][C_0]^n}{[S_0][C_0](\sum_{i=1}^{n} k_i + [C_0] \sum_{j=1}^{m} k_j)} \qquad (10)$$

Equation (10) can therefore be used to evaluate the initial rate constant for the formation of A, in the following manner:

$$k_A[S_0][C_0]^n = \begin{pmatrix} \text{initial slope} \\ \text{of the OPE} \end{pmatrix}[S_0][C_0]$$
$$\times (\sum_{i=1}^{n} k_i + [C_0] \sum_{j=1}^{m} k_j). \quad (11)$$

This can be further simplified since in this work $[C_0]$ was maintained at 1 atm. Consequently,

$$k_A[S_0] = \begin{pmatrix} \text{initial slope of the OPE} \\ \text{for product A} \end{pmatrix}$$
$$\times (\sum_{i,j=1}^{n+m} (k_i + k_j)[S_0]). \quad (12)$$

Also note that, from the conservation of matter, the following equation must hold:

$$2 \sum_{i=1}^{n} (r_i) \underset{\substack{\text{second-order} \\ \text{reactions}}}{} + \sum_{j=1}^{m} (r_j) \underset{\substack{\text{first-order} \\ \text{reactions}}}{}$$
$$= \begin{pmatrix} \text{total rate of loss} \\ \text{of cumene } (-r_c) \end{pmatrix}, \quad (13)$$

in which case, from Eqs. (10) and (13), we arrive at

$$2 \sum_{i=1}^{n} \begin{pmatrix} \text{initial slope} \\ \text{of the OPE} \end{pmatrix}_{\substack{\text{second-order} \\ \text{reactions}}}$$
$$+ \sum_{j=1}^{m} \begin{pmatrix} \text{initial slope} \\ \text{of the OPE} \end{pmatrix}_{\substack{\text{first-order} \\ \text{reactions}}} = 1.0. \quad (14)$$

EXPERIMENTAL

A tubular packed-bed laboratory reactor containing a highly active La-exchanged Y-type zeolite catalyst was used in this study to generate selectivity data for all the primary products listed in Table 1. A 17-fold range of cat./oil ratios and a 20-fold range of catalyst times on stream ensured that sufficient selectivity data were obtained at each of the three reaction temperatures studied: 360, 430, and 500°C. A more complete discussion of the apparatus and experimental procedure is presented elsewhere (1, 3).

RESULTS

Samples of selectivity data for benzene, propylene, and cymene have been presented previously (1). An examination of the Optimum Performance Envelopes shown there reveals that these data follow a trend consistent with that expected for primary stable reaction products in that the selectivity appears to be linear over the range of conversion studied.

The m- and p-diisopropyl benzene selectivities demonstrate behavior typical of primary unstable reaction products (1).

The remaining primary reaction products which include n-propyl benzene, butene, and isobutene have been found to arise from both primary and secondary reactions. The Optimum Performance Envelopes for these compounds were presented previously (1) and the corresponding initial selectivities of all primary products are tabulated here in Table 1. It should be pointed out that Table 1 does not include the selectivities for either ethyl benzene or propyl-

Temperature (°C)	Compound	Order of reaction	Catalyst mesh size	
			100/140	70/80
500	Benzene	1	0.933	0.937
	n-Propyl benzene	1	0.0030	0.0038
	Cymene	2	0.0018	0.0010
	m-Diisopropyl benzene	2	0.0135	0.0140
	p-Diisopropyl benzene	2	0.0070	0.0068
	Isobutene	2	0.0020	0.0018
	Butene	2	0.0038	0.0037
	Total selectivity		0.9925	0.9954
430	Benzene	1	0.870	0.865
	n-Propyl benzene	1	0.0031	0.0041
	Cymene	2	0.0033	0.0032
	m-Diisopropyl benzene	2	0.0335	0.0366
	p-Diisopropyl benzene	2	0.0199	0.0205
	Isobutene	2	0.0040	0.0040
	Butene	2	0.0048	0.0047
	Total selectivity		1.0041	1.0071
360	Benzene	1	0.650	0.650
	n-Propyl benzene	1	0.0028	0.0029
	Cymene	2	0.0130	0.0123
	m-Diisopropyl benzene	2	0.0850	0.0800
	p-Diisopropyl benzene	2	0.0580	0.0640
	Isobutene	2	0.0095	0.0095
	Butene	2	0.0072	0.0073
	Total selectivity		0.9982	0.9991

ene. In the reaction network presented in Ref. (1) it can be seen that initially these compounds are the products of reactions which produce cymene and benzene, respectively. Hence their inclusion here would be redundant. In addition, it is clear that benzene is formed as a product in the formation of diisopropyl benzene from cumene, in the formation of butene, and in the dominant dealkylation reaction. Consequently, it is necessary to subtract the selectivity for the butenes and for diisopropyl benzenes from the "total" benzene selectivity in order to obtain the selectivity for benzene due to the dealkylation reaction alone. The benzene selectivities reported in Table 1 show such corrected quantities.

With the initial slopes listed in Table 1, the initial rate constants for the formation of the primary products can be determined from Eq. (12) if the overall initial rate of conversion of cumene is known. Unfortunately, the kinetics of this overall initial rate of cumene conversion are very complex in our system and an alternate approach has to be used. In a previous paper (3) the initial rate constant for the dealkylation reaction was calculated. This is the initial rate constant for the formation of benzene by dealkylation and, in that sense, is connected with the selectivity for benzene listed in Table 1. With this estimate of $k[S_0]$ and the initial selectivity for benzene due to dealkylation, the overall rate of cumene conversion can be easily determined using Eq. (12). Subsequently all the other rate constants can be determined using the rate of overall cumene conversion

TABLE 2

Initial Rate Constant for the Overall Loss of Cumene as Determined from the Initial Rate Constant for Benzene Formation (3) and the Initial Benzene Selectivity

Temperature (°C)	Mesh size	Benzene initial selectivity	Benzene $k_B[S_0]$ (mole/g sec)	Overall initial rate of cumene conversion (mole/g sec)
500	100/140	0.933	0.0475	0.0509
	70/80	0.937	0.0475	0.0507
430	100/140	0.870	0.0113	0.0130
	70/80	0.865	0.0106	0.0122
360	100/140	0.650	0.0017	0.0026
	70/80	0.650	0.0017	0.0026

thus obtained. Values obtained in this way for the total rate of cumene conversion at the various reaction temperatures are shown in Table 2. Next, using Eq. (12), the values for the rate of cumene conversion from Table 2, and the initial slopes from Table 1, we have calculated the initial rate constants for all the primary products under the conditions studied. These results are shown in the form of Arrhenius plots in Fig. 2. The corresponding activation energies and preexponential factors for the formation of all primary products are tabulated in Table 3. The orders of the reactions and the nature of the active sites involved (1) are also shown.

DISCUSSION

Kinetics of Formation of the Primary Products of Cumene Cracking

According to Eq. (14), the sum of the initial selectivities for first-order reactions plus twice the sum for second-order reactions should equal 1. This condition is fulfilled for all cases studied here as shown by the summations in Table 1, leaving little doubt that all the important primary products have been accounted for. With this established we can proceed with the kinetic analysis of these products.

The Consequences of the Observed Kinetics of Minor Product Formation

It appears that the activation energies listed in Table 3 (except for the dealkylation reaction) are the first of their kind ever reported. Consequently, a comparison
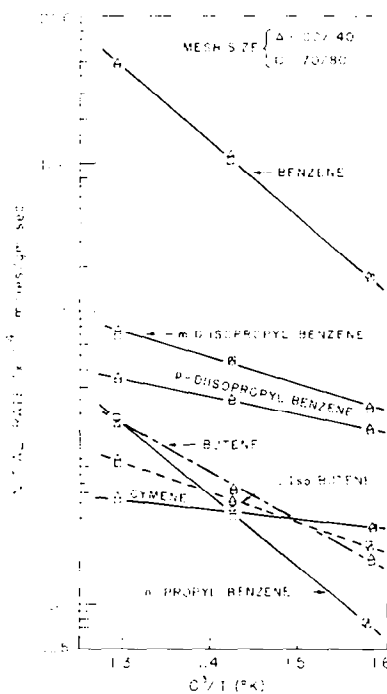

FIG. 2. Arrhenius plots for the initial rates of formation of benzene, n-propyl benzene, m- and p-diisopropyl benzene, isobutene and butene, and cymene.

TABLE 3

Activation Energies and Frequency Factors for the Initial Rate Constants for the Formation of the Primary Products of the Cumene Reaction on 100/140-Mesh Catalyst

Compound	Order of reaction	Type of active site[a]	Activation energy (kcal/mole)	Frequency factor $\times [S_0]$ (mole/g sec)
Benzene	1	B	22.5	1.20×10^6
n-Propyl benzene	1	L	21.6	1.94×10^2
m-Diisopropyl benzene	2	B	7.9	1.26×10^{-1}
p-Diisopropyl benzene	2	B	6.0	1.87×10^{-2}
Cymene	2	L	6.8	7.08×10^{-3}
Isobutene	2	L + B	9.8	5.73×10^{-2}
Butene	2	L + B	16.3	1.37×10^{-1}

[a] B represents Brønsted acid site, while L represents Lewis acid site.

with other values from the literature cannot be made. However, these estimates of the activation energies and frequency factors do furnish some insight into the various processes that occur on the catalyst surface and provide additional support for the corresponding chemical reaction mechanisms presented earlier (1).

The activation energies for the first-order reactions leading to the dealkylation and isomerization of cumene are clearly in a class by themselves. An activation energy for n-propyl benzene formation, which is nearly equal to that for cumene dealkylation, suggests that the transition state is similar for both reactions. However, in view of the fact that a different mechanism has been proposed for the initial formation of the carbonium ion in each of these reactions (1), we must suppose that the formation of the ion is not rate limiting and that almost complete bond breaking occurs in the isomerization of cumene to n-propyl benzene. The lower activation energies for the remaining reactions, all of them second-order disproportionations, suggest that these involve concerted mechanisms involving the transfer of an alkyl group from one cumene molecule to a second cumene molecule at little cost in energy.

Turning to more detailed considerations we see that the relative activation energies for butene and isobutene are also consistent with the mechanisms suggested for their formation (1). These compounds are thought to be the result of a methyl transfer from an isopropyl group of one cumene molecule to an isopropyl chain on a second cumene molecule. According to the relative activation energies for these compounds, such a transfer requires more energy than the corresponding addition to a benzene ring as required, for example, in cymene production. In addition, we find that the transfer of the methyl group to an α carbon of the isopropyl group (the tertiary carbon atom) to produce isobutene is energetically more favorable than a similar transfer to a primary carbon with the consequent formation of butene. Furthermore it seems that the subsequent cracking reaction is not rate limiting which in turn confirms our postulate that the butyl benzenes are unstable intermediates (1).

Further insight into the butene reactions can be gained from an analysis of the frequency factors shown in Table 3. Examining this table we find that the frequency factor per reactive carbon atom in the alkyl chain is 5.7×10^{-2} sec⁻¹ for isobutene. This is nearly equal to that for butene formation which is calculated to be $0.5(13.7 \times 10^{-2})$ or 6.8×10^{-2} sec⁻¹ per reactive carbon atom. (The factor of 0.5 has been used because there are two carbon

atoms available for butene formation whereas only one is available for isobutene formation.) Since the frequency factors for both butene reactions are nearly the same, we conclude that the selectivity for either butene or isobutene is mainly the consequence of an energetic effect, with the isobutene being the energetically favored product.

In a similar comparison of p- and m-diisopropyl benzene we find the frequency factor for the *meta* isomer to be $0.5(12.6 \times 10^{-2})$ or 6.3×10^{-2} sec^{-1} per reactive carbon atom, whereas that for p-diisopropyl benzene is only 1.87×10^{-2} sec^{-1}. As these differ by more than a factor of 3, and because the activation energies are also different, it appears that diisopropyl benzene formation is influenced by both energy and entropy considerations, with p-diisopropyl benzene being favored by energy requirements while the *meta form* is favored by the entropy (or configurational) requirements. Furthermore, because of the difference in both activation energy and frequency factor, the relative rates of formation of the two isomers will be temperature dependent, as will be the ratio of their initial yields. The yield ratio of *meta* to *para* of approximately 2, found in this study at 500°C, will not hold over a wide range of temperatures. In fact at room temperature the ratio would be approximately 0.3.

Unfortunately, since $[S_0]$, the concentration of active sites on the catalyst, is an integral component of the frequency factors listed in Table 3, further analysis is somewhat restricted. In the case of the reactions initiated through proton addition, $[S_0]$ represents the concentration of Brønsted acid sites. On the other hand, for hydride extraction reactions, $[S_0]$ is the concentration of Lewis acid sites. Since these two concentrations are different and unknown for this catalyst, comparisons of frequency factors such as that made above for the diisopropyl benzenes and butenes cannot be carried out for most other pairs of compounds listed in Table 3. We note in passing that the concentration of Lewis acid sites is thought to be significantly smaller than the concentration of Brønsted sites at the temperatures studied in this work.

Looking at the overall picture which emerges from the data presented in Table 3, one gets the impression that the two monomolecular reactions form one set, and the bimolecular reactions, another. This occurs despite the fact that in each set there are two subsets: the Lewis acid- and the Brønsted acid-catalyzed reactions. What can be deduced from all the considerations discussed above is therefore the following.

The formation of a carbonium ion by either type of site is probably not rate limiting; otherwise the same activation energy would be expected to be observed for all the products of a given site. The carbonium ions, once formed, can decompose, rearrange, or undergo a bimolecular disproportionation with a neutral molecule. It appears that the decomposition (cracking) reaction and the rearrangement (to n-propyl benzene) require about the same amount of energy over and above the endothermicity of the ion formation. This similarity in the activation energies indicates that once a carbonium ion is formed its rearrangement requires almost as much energy as its complete decomposition, suggesting that the rearrangement involves almost complete decomposition of the ion.

Similarly in the case of disproportionation reactions, the ions, once formed, react with an activation energy which is dependent only on the type of reaction and is independent of the source of the reacting ion.

CONCLUSIONS

The kinetic parameters of three transalkylation reactions and an isomerization which occur when pure cumene is reacted

in the presence of a LaY catalyst have been determined. Consideration of the values of these parameters leads us to conclude the following.

(a) The isomerization of cumene to n-propyl benzene proceeds via a transition state which requires almost complete rupture of the side chain to the benzene ring bond.

(b) The addition of a methyl from the side chain of one cumene molecule to the benzene ring of another to produce cymene requires less energy than the insertion of the same methyl into the isopropyl group of the second cumene molecule.

(c) The insertion of a methyl group from the isopropyl of one cumene molecule into the isopropyl group of the second cumene requires much less energy in the case of addition to the α carbon than it does when addition takes place at the terminal (β) carbon.

(d) In the case of the above addition of a methyl to the isopropyl group there is no difference in the entropy required for addition to the α and β carbons.

(e) The disproportionation of two cumenes to produce benzene and diisopropyl benzene leads mainly to the *meta* and *para* isomers.

(f) At and around 500°C the *meta* isomer is the predominant species of diisopropyl benzene formed on LaY.

(g) The formation of the *meta*-diisopropyl benzene is favored by the entropy whereas the formation of the *para* isomer is favored by the energy of activation.

REFERENCES

1. Best, D. A., and Wojciechowski, B. W., *J. Catal.* **47**, 11 (1977).
2. Best, D. A., and Wojciechowski, B. W., *J. Catal.* **31**, 74 (1973).
3. Best, D. A., and Wojciechowski, B. W., *J. Catal.* **47**, 343 (1977).
4. Campbell, D. R., and Wojciechowski, B. W., *Canad. J. Chem. Eng.* **47**, 413 (1969).