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NOTE

The Catalytic Cracking of Cumene Interpreted as a Chain Mechanism

Recent publications on the chain mechanism of catalytic cracking have focused on paraffin cracking (1–3). Before we apply the concepts developed in those papers to olefins, we present the intermediate case of cumene cracking or, more generally, the dealkylation of aromatics. The benzene ring of cumene with its π bonding character suggests that initiation in this case may not involve protolysis as it does in paraffin cracking but proceeds by proton addition to the benzene ring. At the same time, it has been reported that the benzene ring stays intact during the cracking process and dealkylation is the major reaction observed (4, 5).

By examining the product distribution and the initial molar selectivity data of any catalytic cracking reaction, a catalytic cracking chain mechanism can be developed using the principles previously defined (1–3). A chain cracking mechanism in general consists of the following steps (1):

1. Chain initiation reactions. The initiation reactions are assumed to occur on Brønsted acid sites. In the case of cumene this results in the protonation of the feed molecule forming a carbenium ion.

$$\Phi\text{-}C_mH_{2m+1} + BH \rightarrow \Phi_H\text{-}C_mH_{2m+1}{}^+B^- \qquad [1]$$

It is here, in the initiation process, that cumene cracking differs from paraffin cracking. There is no product formed by the initiation reaction; instead, the initial carbenium ion is at steady state with the gas-phase molecules of the feed.

2. Chain propagation reactions. Chain propagation consists of bimolecular reactions between the carbenium ions on the catalyst surface and feed molecules. In cumene cracking, since there is no evident cracking of the benzene ring, chain propagation reactions consist of disproportionations involving the transfer of all or part of the side chain of a cumene molecule to a carbenium ion.

$$\Phi_H\text{-}C_mH_{2m+1}{}^+B^- + \Phi\text{-}C_mH_{2m+1} \rightarrow \Phi\text{-}C_{2m-n}H_{4m-2n+1} + \Phi_H\text{-}C_nH_{2n+1}{}^+B^- \qquad [2]$$

3. Chain-transfer reactions. β-cracking reactions are the agents of chain transfer in all catalytic cracking. They introduce new ionic species into the propagation steps while producing "excess" olefins. In cumene cracking, chain transfer produces propyl ions and benzene.

$$\Phi_H\text{-}C_mH_{2m+1}{}^+B^- \rightarrow \Phi + C_mH_{2m+2}{}^+B^- \qquad [3]$$

4. Chain termination reactions. Chain processes in cracking are terminated when a carbenium ion desorbs to produce an olefin, returning the site to its pristine state as Brønsted acid.

5. Isomerization and coking. We include two further reactions that a carbenium ion may undergo, isomerization and coking. Isomerization involves a skeletal rearrangement of the carbon atoms in the parent carbenium ion:

$$\Phi_H\text{-}C_mH_{2m+1}{}^+B^- \rightarrow \text{i-}\Phi_H\text{-}C_mH_{2m+1}{}^+B^-. \qquad [4]$$

In cumene cracking the initial molar selectivity for coke is much smaller than the molar selectivity for the other products, permitting the use of a simplified coking reaction (1)

$$\Phi\text{-}C_mH_{2m+1} \rightarrow m_K C_xH_y + m_H H_2, \qquad [5]$$

where C_xH_y represents the molecular formula of coke and will serve to balance the stoichiometry using appropriate values for x and y (1).

By writing all appropriate reactions in this manner, we can calculate for each of them a reaction path probability (RPP $= X$) (1). We define an initiation reaction by a subscript **oi**; **ij** is a propagation reaction, **bij** a β-cracking reaction, **ki** a coking reaction, and **di** a desorption step. Calculation of the RPPs (i.e., the X's) using experimentally obtained initial selectivities makes it possible to quantify the conversion due to the various reactions occurring in the proposed mechanism. It also allows calculation of theoretical product formation probabilities (PFP), isomerization probabilities (IC_m), individual reaction rates (IRR), kinetic chain length (KCL), and so on (1).

We write the experimental initial molar selectivity of each product in terms of a linear combination of the RPP which leads to its formation and consumption. The coefficients of each RPPs expression stem from the stoichiometry of each of the proposed reactions. Since these equations represent a mass balance for each species, there will be as many equations as there are products.

To solve for the RPPs we chose to use the program GAMS. Use of its constraint features guarantees a solution for all X such that $0 \leq X \leq 1$.

The mechanism of the catalytic cracking of cumene is shown in Table 1, with an RPP value assigned to each reaction. The equations used to calculate the RPPs are shown in Table 2. This mechanism accounts for all likely product-

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TABLE 1

The Chain Mechanism of Cumene Cracking

Reaction	RPP
ϕ-C_3H_7 + BH $\rightleftharpoons$ ϕH-$C_3H_7{}^+B^-$	X_{00}[a]
ϕ_H-$C_3H_7{}^+B^- \rightarrow \phi_H{}^+B^-$ + C_3H_6	X_{03}
ϕ_H-C_3H_7 + B$^- \rightarrow \phi$ + $C_3H_7{}^+B^-$	$X_{0(\phi)}$
$C_3H_7{}^+B^-$ + ϕ-$C_3H_7 \rightarrow \phi_H$-$(C_3H_7)_2{}^+B^-$	$X_{3(\phi3)}$
ϕ_H-$C_3H_7{}^+B^-$ + ϕ-$C_3H_7 \rightarrow \phi$-$(C_3H_7)_2$ + $\phi_H{}^+B^-$	$X_{(\phi3)3}$
ϕ_H-$C_3H_7{}^+B^-$ + ϕ-$C_3H_7 \rightarrow CH_3$-ϕ-C_3H_7 + ϕ_H-$C_2H_5{}^+B^-$	$X_{(\phi3)1A}$
ϕ_H-$C_3H_7{}^+B^-$ + ϕ-$C_3H_7 \rightarrow \phi$-C_4H_9 + ϕ_H-$C_2H_5{}^+B^-$	$X_{(\phi3)1B}$
ϕ_H-$C_3H_7{}^+B^- \rightarrow$ i-ϕ_H-$C_3H_7{}^+B^-$	$X_{(\phi3)0}$
$C_3H_7{}^+B^-$ + $\phi \rightarrow \phi_H$-n$C_3H_7{}^+B^-$	X_{33}[b]
ϕ_H-$C_2H_5{}^+B^-$ + ϕ-$C_3H_7 \rightarrow CH_3$-ϕ-C_2H_5 + ϕ_H-$C_2H_5{}^+B^-$	$X_{(\phi2)1}$[c]
$C_3H_7{}^+B^- \rightarrow C_3H_6$ + BH	d_3
$\phi_H{}^+B^- \rightarrow \phi$ + BH	d_ϕ
ϕ_H-$C_2H_5{}^+B^- \rightarrow \phi$-$C_2H_5$ + BH	$d_{(\phi2)}$
ϕ_H-$C_3H_7{}^+B^- \rightarrow \phi$-n$C_3H_7$ + BH	$d_{(\phi3)}$
CH_3-ϕ_H-$C_3H_7{}^+B^- \rightarrow CH_3$-$\phi$-$C_3H_7$ + BH	$d_{(\phi4)}$
ϕ_H-$(C_3H_7)_2{}^+B^- \rightarrow \phi$-$(C_3H_7)_2$ + BH	$d_{(\phi6)}$
ϕ-$C_4H_9 \rightarrow \phi$ + C_4H_8	

[a] This reaction is not included in the analysis.
[b] This reaction is believed to occur only at high reaction temperatures.
[c] Ethyl toluene had a strange selectivity graph and was included as a primary product for this analysis.

forming reactions, including those for products not reported in the initial molar selectivities found in the original works (4–8). Note the inclusion of the reaction (ϕ2)1, the propagation reaction forming ethyl toluene. Although no initial selectivity is reported for ethyl toluene in most works, the solution of the RPP equations *required* inclusion of this reaction, in order to establish a reasonable solution. The original authors recognized ethyl toluene as an initial product but, because they had difficulty in evaluating its initial selectivity (4, 7), they did not quantify this value.

Reactions 03, 33, and 3(ϕ3) are not included in the mechanism. In the original work (4) an argument was made as to why these reactions do not occur. Upon inspection, it can be seen that 33 and 3(ϕ3) are clearly secondary reactions. Reaction 03 is not included since there is general agreement (4, 5) that benzene is released to the gas phase on the dealkylation of the protonated cumene. Without these exclusions, the solution of the mechanism yields physically meaningless results. We believe that this confirms the validity of the mechanism proposed. Moreover, X_{03} and $X_{0(\phi)}$ are *confounded* variables; if both are left in the mechanism they cannot be separated and only their sum is calculated. X_{33} and $X_{(\phi3)0}$ exhibit similar behaviour, although these two variables are not, in the strictest sense, confounded.

TABLE 2

The RPP Defining Equations

Product	Equation	Selectivity
Benzene	$X_{03} + X_{0\phi} + X_{(\phi3)1B} + X_{(\phi3)3} - X_{33} =$	O_ϕ
Propylene	$X_{03} + X_{0\phi} - X_{3(\phi3)} - X_{33} =$	O_3
n-Propyl benzene	$X_{(\phi3)0} + X_{33} =$	$O_{(\phi3)}$
Cymene	$X_{(\phi3)1A} =$	$O_{(\phi4)}$
Diisopropyl benzene	$X_{3(\phi3)} + X_{(\phi3)3} =$	$O_{(\phi6)}$
Butenes	$X_{(\phi3)1B} =$	O_4
Ethyl benzene	$X_{(\phi3)1A} + X_{(\phi3)1B} + X_{(\phi2)1} =$	$O_{(\phi2)}$[a]

[a] O_x represents an olefin with x carbons. ϕ represents the benzene ring.

To improve the solution of the sensitive matrix involved in this type of interpretation, we undertook to correct the reported mass balances using the following techniques of renormalization:

1. for LaY, HY, and partially exchanged NaLaY, the mass balance was corrected by introducing ethyl benzene in an amount required to bring the reported weight selectivity total to 1.00; the molar selectivities were adjusted accordingly;
2. for amorphous-silica, the reported weight selectivity total was normalized to 1.00; and the molar selectivities were adjusted accordingly;
3. for the HZSM-5 data, no correction was necessary.

With these corrections, good results were obtained when fitting the mechanism to the data using the coefficient matrix in Table 2. This correction of literature data should serve as a warning that our new procedure, in this as in other cases (9), makes rigorous demands on the accuracy of the data collected.

No correction was required for the data of Dadyburjor (10), who studied cumene cracking in a stream of helium "carrier." The effects of such dilution are not trivial and have been described elsewhere (3). An assumption had to be made in dealing with the propylene yields, since Dadyburjor reports no analysis for propylene. The "gas" reported in (10) was assumed to be propylene. With this estimate of the propylene yield, the mass balance was found to be good. Data for pulse number one in Dadyburjor's data were used to give an estimate of initial selectivities.

In Table 3, it can be seen that our solution is as accurate as experimental error will allow, for LaY at all temperatures. For HY, partially exchanged NaLaY, and amorphous-silica, comparable accuracy was obtained only at the higher temperatures. An inspection of the mass balances, based on the molar selectivities reported (5, 7), reveals a large experimental error at the lower temperatures; at these temperatures our solution exhibits a significant "infeasibility," showing that experimental data containing a large error cannot be corrected by the renormalization methods used.

In agreement with the conclusions in the original work (4), the KCL (there it was measured as the contribution of disproportionation reactions) increases as the reaction temperature is lowered, indicating that chain propagation processes in cumene cracking are more prominent at lower temperatures and therefore have a lower activation energy than "cracking." The calculated activation energies in Table 3 indicate good agreement with previous interpretations (4, 5, 7). Detailed inspection of the results in Table 3

TABLE 3

Summary of RPP Values and Apparent Activation Energies Calculated

RPP		LaY		Ea	Ref. Ea(4)
	360	430	500		
$X_{0\phi}$	0.64	0.87	0.93	97.4	94.2
$X_{(\phi3)0}$	0.003	0.003	0.003	86.4	90.4
$X_{(\phi3)3}$	0.143	0.053	0.003	29.4	29.3
$X_{(\phi3)1A}$	0.013	0.003	0.003	29.9	28.5
$X_{(\phi3)1B}$	0.017	0.009	0.006	56.0	54.6
$X_{(\phi2)1}$	0.017	0.013	0.013	78.4	—
Infeasibility	0.014	0.028	0.004		
KCL	1.56	1.15	1.07		
RPP		HY		Ea	Ref. Ea
	360	430	500		
$X_{0\phi}$	0.655	0.84	0.92	96.4	—
$X_{(\phi3)0}$	0.002	0.001	0.001	65.6	—
$X_{(\phi3)3}$	0.204	0.077	0.024	24.6	—
$X_{(\phi3)1A}$	0.002	0.00048	0.00015	11.2	—
$X_{(\phi3)1B}$	0.004	0.002	0.001	46.2	—
$X_{(\phi2)1}$	0.082	0.05	0.031	58.2	—
Infeasibility	0.22	0.079	0.005		
KCL	1.53	1.19	1.09		
RPP		NaLaY		Ea	Ref. Ea(7)
	400	450	500		
$X_{0\phi}$	0.75	0.83	0.93	96.1	103.1
$X_{(\phi3)0}$	0.002	0.002	0.002	86.8	95.8
$X_{(\phi3)3}$	0.131	0.084	0.036	31.4	35.0
$X_{(\phi3)1A}$	0.002	0.0008	0.0005	26.4	24.2
$X_{(\phi3)1B}$	0.004	0.002	0.002	56.2	53.0
$X_{(\phi2)1}$	0.017	0.015	0.011	68.2	—
Infeasibility	0.168	0.109	0.045		
KCL	1.33	1.21	1.07		
RPP		AmSi-25		Ea	Ref. Ea
	400	450	500		
$X_{0\phi}$	0.733	0.901	0.937	65.5	—
$X_{(\phi3)0}$	0.003	0.003	0.004	66.3	—
$X_{(\phi3)3}$	0.108	0.044	0.025	15.6	—
$X_{(\phi3)1A}$	0	0	0	—	—
$X_{(\phi3)1B}$	0.003	0.003	0.002	46.9	—
$X_{(\phi2)1}$	0.013	0.009	0.008	44.0	—
Infeasibility	0.052	0.024	0.015		
KCL	1.36	1.11	1.07		
RPP		AmSi-13		Ea	Ref. Ea
	400	450	500		
$X_{0\phi}$	0.808	0.916	0.934	62.5	—
$X_{(\phi3)0}$	0.003	0.004	0.004	66.9	—
$X_{(\phi3)3}$	1.122	0.05	0.025	12.2	—
$X_{(\phi3)1A}$	0	0	0	—	—
$X_{(\phi3)1B}$	0.004	0.003	0.002	38.2	—
$X_{(\phi2)1}$	0.011	0.008	0.006	40.7	—
Infeasibility	0.126	0.061	0.009		
KCL	1.24	1.09	1.07		

RPP	NaHY(10)	
	Catalyst 1	Catalyst 2
$X_{0\phi}$	0.979	0.99
$X_{(\phi3)0}$	0	0
$X_{(\phi3)3}$	0	0
$X_{(\phi3)1A}$	0.004	0.002
$X_{(\phi3)1B}$	0	0
$X_{(\phi2)1}$	0.000397	0.0000673
Infeasibility	0.007	0.003
KCL	1.02	1.01

reveals that the calculated RPP values make excellent physical sense and can be shown to produce the same results as those given in previous interpretations of the initial selectivity data.

The results for the more recent HZSM-5 data were very pleasing and may be the most convincing agrument for this mechanism. By entering this selectivity data into the equations used for interpreting all the aforementioned data, the results show that only monomolecular processes are active here. This is exactly what was proposed in the original work (6) and is attributed to stearic hinderence in the smaller pores of the HZSM-5 catalyst.

Dadyburjor's data show that all bimolecular disproportionation reactions have been suppressed. The influence of seemingly inert diluents on the mechanism of cracking has now been amply demonstrated (3) and this result is strictly in keeping with the observations in these other systems.

By applying the chain mechanism developed by Zhao *et al.* (1) to data previously reported on cumene cracking, the same interpretation of the mechanism as that which was obtained using more traditional methods of interpretation (4–8) were extracted. In this simple reaction, one can readily see the reasons behind the traditional interpretation. The fact that the matrix algebra used to quantify this reaction from the perspective of chain mechanism cracking gives the same results as the traditional methods, plus its ability to identify shortcommings in the data, we take to indicate that the application of the chain mechanism postulates and methods of quantification will lead to reasonable results not only here but in catalytic cracking reactions in general.

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