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Paraffin Dehydrocyclization. Competitive Conversion of Paraffins and Naphthenes

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The competitive conversion of several naphthene–paraffin mixtures was studied over supported metal and metal oxide dehydrocyclization catalysts. The conversion of each component was not simply the additive conversion of the pure components. Rather, it was found that for equal molar naphthene and paraffin mixtures the conversion was on a one-to-one basis. A change in paraffin–naphthene mole ratio resulted in a similar change in the relative conversion. The results at atmospheric pressure are consistent with a mechanism in which the adsorption of naphthene and paraffin are equal and the adsorption is the slow step for the reaction. It appears that the relative conversion is dependent on the hydrogen partial pressure; increasing the hydrogen pressure favors an increase in the relative naphthene conversion. The results eliminate the contribution of a gas phase naphthene in the dehydrocyclization mechanism.

INTRODUCTION

Most paraffin dehydrocyclization studies have been done using a pure compound or a complex mixture such as a naphtha where complete analysis of the product was not possible. Some competitive conversions of naphthenes have been reported and it appears that the conversion may be more complicated than merely the additive rate for the pure components (*1*). Only a few reports have appeared concerning the competitive conversion of a paraffin–naphthene mixture; these have usually stressed aromatics formation rather than reactant conversion (*2*). The present study was undertaken to learn whether the conversion for the mixture could be accounted for by the rates for the pure components. In addition, information could be obtained concerning the participitation of gas phase naphthenes, proposed as intermediates in some reaction mechanisms (*3*), in the dehydrocyclization mechanism.

EXPERIMENTAL METHODS

The reaction was carried out in a conventional flow apparatus described previously (*4*). Runs were carried out at atmospheric pressure, LHSV 0.3, 482°C, and without carrier gas unless noted otherwise in the Results Section. Liquid samples were collected at intervals and analyzed by gas chromatography using a Carbowax 20M column. Thus, the points presented in the plots in the Results Section are the average conversion during the time interval between samples rather than the actual conversion at a given time.

With the exception of ethylcyclohexane, which was prepared by the hydrogenation of ethylbenzene, the hydrocarbons were purchased from the Chem-Samp-Co or Phillips and were used without further purification.

Catalysts

Pt–Al_2O_3–K. "Nonacidic" alumina was impregnated with chloroplatinic acid; the chlorine was reduced to a low level by washing the reduced catalyst with ammonium hydroxide [see Ref. (*4*) for details of the preparation]. The catalyst contained 0.6 wt % Pt; less than 0.05 wt % Cl; and 1 wt % K.

Pt–Cl–Al_2O_3–K. This catalyst was the same as Pt–Al_2O_3–K except that the chlorine added as chloroplatinic acid was not removed by washing. The catalyst contained 0.6 wt % Pt and 0.6 wt % Cl which corresponds to $PtCl_6$.

Rh-Cl-Al_2O_3-K. The same as the Pt–Cl catalyst except $(NH_4)_3RhCl_6$ was used for the impregnation. The catalyst contained 0.55 wt % Rh.

Cr_2O_3-Al_2O_3. Alumina from the hydrolysis of aluminum isopropoxide was impregnated with chromic acid (*5*). The catalyst, after calcination at 600°C, contained 13 wt % Cr.

Ni-Sn-Cl-Al_2O_3-K. An ethanol solution of $NiCl_2$ and $SnCl_2$ (Ni:Sn ratio of 1:4) was used to impregnate the "nonacidic" alumina. The final catalyst contained 0.6 wt % Ni.

RESULTS

The relative conversion of an ethylcyclohexane (ETCH) and *n*-octane mixture over Pt–Al_2O_3 is presented in Table 1. Pure ETCH, as well as dimethylcyclohexane (DMCH) and cyclohexane (CH), was completely dehydrogenated to the aromatic when passed over the Pt catalyst using the same conditions and nearly complete conversion of the naphthene occurred at temperatures as low as 350°C. It is obvious that the naphthene conversion is lower when mixed with *n*-octane since, at 482°, less than

TABLE 1

EFFECT OF HYDROGEN PARTIAL PRESSURE ON THE CONVERSION OF *n*-OCTANE ETHYLCYCLOHEXANE MIXTURES OVER Pt AND Cr_2O_3 CATALYSTS AT 482°C AND ATMOSPHERIC PRESSURE

Initial reaction mixture			Time (min)	Conv.[a] (wt %)	ECH/*n*-C_8 conversion	ECH/*n*-C_8 Conv. corrected[b]
$P_{n\text{-}C_8}$	P_{ECH}	P_{H_2}				
			Platinum			
0.32	0.28	0.40	36	62	1.12	1.24
			81	43	1.21	1.34
			127	33	1.33	1.47
			175	28	1.23	1.36
			226	24	1.25	1.38
0.53	0.47	0.00	42	65	1.12	1.24
			93	46	1.25	1.38
			145	35	1.27	1.41
			195	29	1.21	1.34
			235	20	1.43	1.58
0.29	0.71	0.00	34	73	3.14	1.27
			76	51	3.11	1.26
			135	32	3.84	1.51
			191	28	3.54	1.43
			Chromia			
0.30	0.30	0.40	36	78	1.35	1.35
			95	79	1.38	1.38
			157	75	1.40	1.40
			223	74	1.44	1.44
0.50	0.50	0.00	33	69	1.57	1.57
			92	65	1.69	1.69
			153	65	1.65	1.65
			221	63	1.91	1.91

[a] Total conversion of *n*-octane and ethylcyclohexane is based on the analysis of the liquid products.

[b] Corrected values are the experimental values for the ECH/*n*-C_8 conversion divided by the mole ratio of ECH/*n*-C_8 in the initial reaction mixture.

complete conversion was obtained. Increasing the initial hydrogen partial pressure from zero to 0.40 atm did not influence the relative conversion for the ETCH–*n*-octane mixture over Pt–alumina. Increasing the ETCH mole ratio from 1 to 2.3 caused a corresponding increase in the ratio of naphthene converted from 1.25 to 3.1 for the first sample. Allowing for the change in molar concentrations of the paraffin and naphthene, both the 1.0 and the 2.3 naphthene–paraffin mixtures had the same relative conversion of about 1.25 at the early time on stream and appeared to remain nearly constant with time. Thus, for this mixture at 482° the naphthene–paraffin conversion is only slightly greater than a one-to-one basis.

The total conversion of the naphthene–paraffin mixture with time is very similar to the conversion obtained with pure *n*-octane under the same conditions (*4*). For example, with the mixture the total conversion decreased from about 60% at the early time on stream to about 25% at 200 min on stream. For the same conditions with pure *n*-octane, the conversion decreased from about 50 to 20% at about 200 min on stream. Thus, the total conversion is far less than the separate conversion for the paraffin and the naphthene.

The relative conversion for the naphthene–paraffin mixture is very dependent on the temperature. Table 2 presents data for the conversion of mixtures of *n*-hexane–CH and *n*-octane–ETCH at 400 and 482°C. While the ratio for 400° has a large experimental error due to the low conversion of the *n*-paraffin and the high conversion of the naphthene, it is obvious that the naphthene was much more reactive than the paraffin at this temperature. But increasing the temperature to 482° decreased the relative amount of naphthene converted from about 20 to only about 1.2 times the paraffin conversion. Furthermore, the total amount of naphthene conversion was decreased by increasing the temperature.

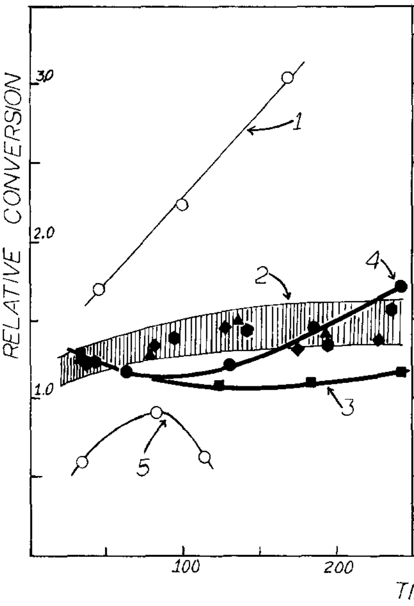
The conversion of *n*-octane–ETCH mixtures over several catalysts is presented in Fig. 1. The relative conversions, with the exception of the Rh and the thiophene promoted Ni–Sn catalysts, are very similar for the different catalysts. Similar relative conversions were also obtained for the other naphthene–paraffin mixtures over the other catalysts studied (Figs. 2–4). The differences in the relative conversions at 482° for the various mixtures and catalysts are small when compared to the relative conversion at 400°C. Thus, the general result is that at 482° there is no gross differences for the naphthene–paraffin mixtures and the relative conversion is about a one-to-one basis.

TABLE 2

Influence of Temperature on the Competitive Conversion of Ethylcyclohexane and *n*-Octane Over Pt–Al_2O_3 at 482°C Without Added Hydrogen

	400°C		482°C	
	Time on stream (min)	Relative conversion[a]	Time on stream (min)	Relative conversion[a]
Ethylcyclohexane–*n*-octane	29	25	42	1.24
	72	50	93	1.38
	116	25	145	1.41
	168	18	195	1.34
	197	22	235	1.58
Cyclohexane–*n*-hexane	45	19	49	0.94
	110	92	109	1.31
	180	20	164	1.26

[a] Relative conversion was the ratio of naphthene:paraffin conversions corrected to an equal molar basis; the value at 400°C is only approximate due to the low conversion of the paraffin and the high conversion of the naphthene.



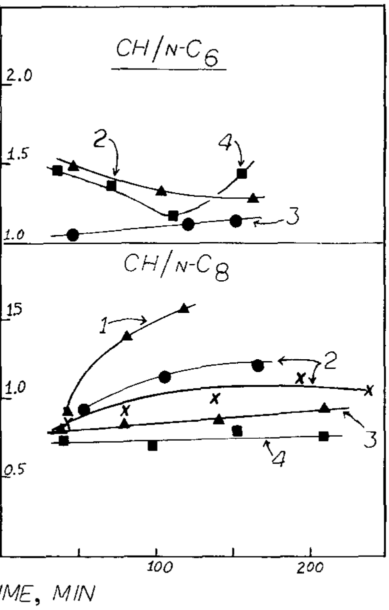
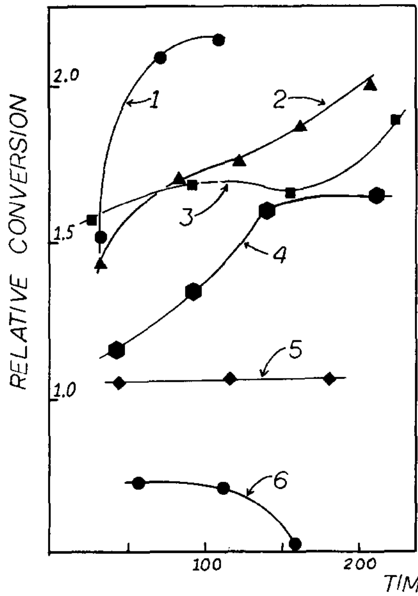


FIG. 1 (left). Relative conversion, ethylcyclohexane/*n*-octane, at 482°C over: (1) Rh-Al_2O_3; (2) three runs over Pt-Al_2O_3; (3) Co-ZrO_2; (4) Ni-Sn-Al_2O_3; and (5) Ni-Sn-Al_2O_3 with 5% thiophene added to the charge.

FIG. 2 (right). Relative conversion, cyclohexane/*n*-hexane and cyclohexane/*n*-octane, at 482°C over: (1) Rh-; (2) Pt-; (3) Cr_2O_3-; and (4) Co-Mo-Al_2O_3. (Co-Mo-Al_2O_3 was a commercial catalyst from Harshaw).



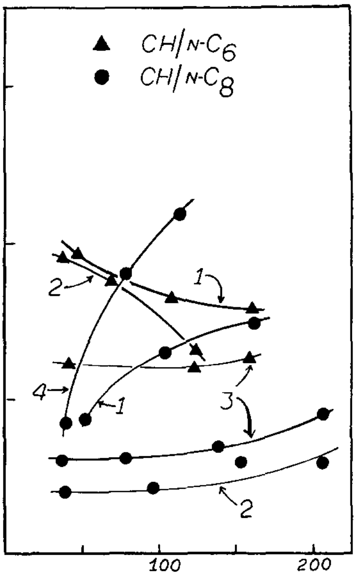


FIG. 3 (left). Relative conversion, dimethylcyclohexane/*n*-octane, at 482°C: (1) *cis*-1,2-DMCH over Pt-Cl-Al_2O_3; (2) *cis*-1,2-DMCH over Pt-Al_2O_3; (3) *cis*-1,2-DMCH over Cr_2O_3-Al_2O_3; (4) *cis*- and *trans*-1,4-DMCH over Pt-Al_2O_3; (5) *cis*- and *trans*-1,2-DMCH over Co-Mo-Al_2O_3; and (6) *cis*- and *trans*-1,4-DMCH over Rh-Al_2O_3.

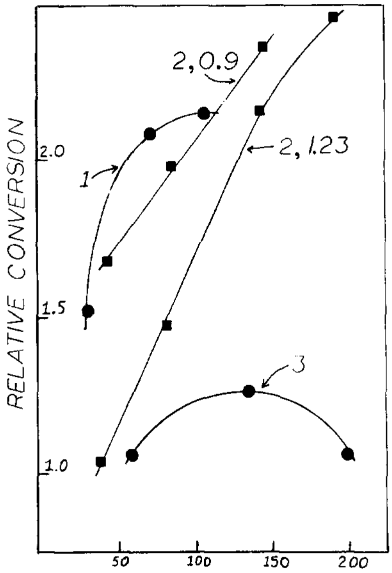
FIG. 4 (right). Relative conversion, cyclohexane/paraffin, at 482°C over: (1) Pt-; (2) Co-Mo-; (3) Cr_2O_3-; and (4) Rh-Al_2O_3.

However, it seems worthwhile to examine these small differences in more detail.

The conversion of the various naphthene–paraffin mixtures over the five catalysts are shown in Figs. 5 through 8. For some catalysts the conversion of the naphthene relative to the paraffin appears to increase as the catalyst remains on stream and ages. However, the relative conversion, even at the longer time on stream, does not approach the higher relative conversion based on the individual rates of naphthene and paraffin conversion. For all catalysts, the naphthene–paraffin conversion ratio is higher for the lower carbon number paraffins; for example, the initial ratio over the Pt catalyst for CH–*n*-octane is about 1 while the initial ratio for CH–*n*-hexane is about 1.5. Likewise, the initial ratio for *cis*-1,2-DMCH–*n*-octane is about 1.5 and for the *cis*-1,2-DMCH–*n*-hexane mixture is about 2.3. Similar trends also are evident for the other catalysts. However, the mixture of methylcyclohexane (MCH)–*n*-pentane does not seem to follow this trend for the two catalysts used (Rh– and Pt–Cl–Al_2O_3–K). The ratio is about 1.5 and 1.0 for the Rh– and Pt–Cl catalysts, respectively; whereas, we would expect this ratio to be even higher than the ratios obtained with *n*-hexane.

The results over the Pt–Al_2O_3–K catalyst can be checked for consistency. The experimental ratio for the conversion of *n*-octane–*n*-hexane was about 1.7. Using the initial relative conversion for the CH–*n*-hexane and CH–*n*-octane mixtures we calculate a *n*-octane–*n*-hexane ratio of 1.5. Using the ratios for *cis*-1,2-DMCH–*n*-hexane and –*n*-octane, the calculated ratio for *n*-octane–*n*-hexane is 1.6. The agreement between the experimental and calculated ratio is not as good for later time on stream and the agreement in the above examples is probably better than we should generally expect.

For the naphthene–*n*-octane mixture the relative ratios give a naphthene relative reactivity order of: CH $<$ ETCH $\simeq$ 1,4-DMCH $<$ 1,2-DMCH. This order is in line with that one would expect based on the pure naphthene conversion (*6*).



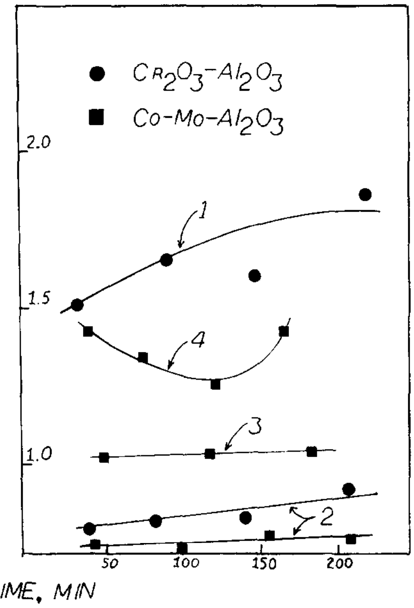
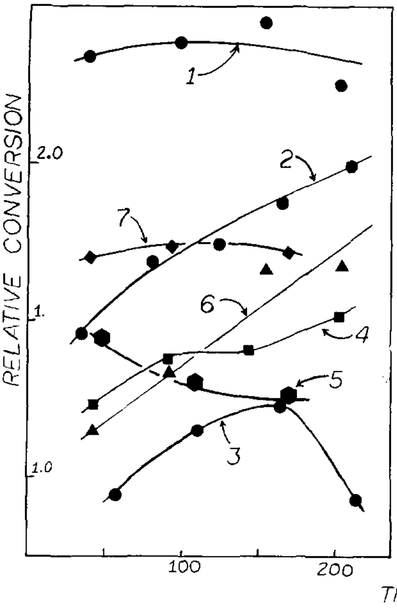


FIG. 5 (left). Relative conversion of naphthene/paraffin mixtures at 482°C over Pt–Cl–Al_2O_3: (1) *cis*-1,2-DMCH/*n*-octane; (2) cyclohexane/*n*-octane, 0.9 and 1.23 mole ratios (the relative conversion for the 1.23 mixture is twice that plotted); (3) cyclohexane/methylcyclopentane.

FIG. 6 (right). Relative conversion of naphthene/paraffin mixtures at 482°C over Cr_2O_3– and Co–Mo–Al_2O_3: (1) *cis*-1,2-DMCH/*n*-octane; (2) cyclohexane/*n*-octane; (3) *cis*- and *trans*-1,4-DMCH/*n*-octane; (4) cyclohexane/*n*-hexane.



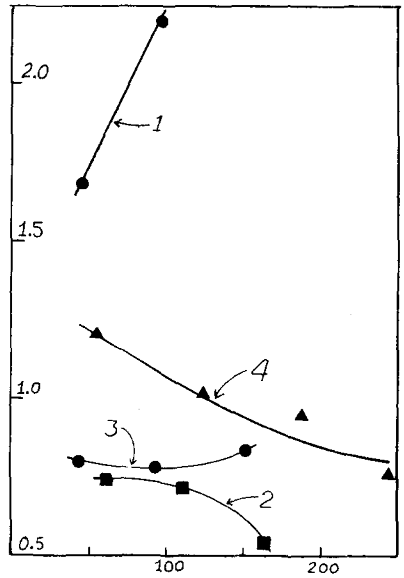


FIG. 7 (left). Relative naphthene/paraffin conversion over Pt–Al_2O_3 at 482°C: (1) *cis*-1,2-DMCH/*n*-hexane; (2) *cis*-1,2-DMCH/*n*-octane; (3) CH/*n*-octane; (4) ETCH/*n*-octane; (5) CH/*n*-hexane; (6) *cis*- and *trans*-1,4-DMCH/*n*-octane; (7) *n*-octane/*n*-hexane.

FIG. 8 (right). Relative naphthene/paraffin conversion over Rh–Al_2O_3 at 482°C: (1) methylcyclohexane/*n*-pentane; (2) *cis*-1,2-DMCH/*n*-octane; (3) cyclohexane/*n*-octane; (4) ETCH/*n*-octane.

The runs described above were made at 1 atm total pressure. Over chromia at this pressure, the relative conversion was influenced by hydrogen partial pressure (Table 1); however, this could be caused by a change in the amount of reduction of the oxide catalyst. At 1 atm the relative conversion was not influenced by hydrogen pressure over the Pt–Al_2O_3 catalyst (Table 1). The relative conversion was different at 1 and 5 atm over Pt–Al_2O_3. For a CH–*n*-octane mixture, the naphthene was completely converted but only about 25% of the *n*-octane was converted (LHSV 1; CH:*n*-octane ratio 1.33; H_2:hydrocarbon ratio 4; total pressure 75 psig; and 500°C). Thus, the naphthene conversion was at least five times that of the paraffin and could have been much higher since the complete conversion of cyclohexane could have occurred at the top of the catalyst bed.

Cyclohexene–*n*-octane (2:1 mole ratio) was converted over a Pt–Al_2O_3–K catalyst at 482°. In contrast to the cyclohexane mixture, cyclohexane was nearly completely converted even after the catalyst had aged so that the conversion of *n*-octane was less than 5%. Thus, even at the early time on stream the relative conversion was at least nine and could have been much higher.

DISCUSSION

The conversion of naphthenes in a naphthene–paraffin mixture is less than expected from the conversion rate of the pure naphthene. Furthermore, it appears that the relative conversion of the naphthene–paraffin mixture varies directly with the molar composition of the mixture; for an equal molar mixture the conversions are nearly on a one-to-one basis. The total conversion does not appear to be strongly influenced by the change in mole ratio provided we have less than complete conversion of the paraffin or naphthene.

The kinetic treatment for surface catalyzed reactions generally assumes that the equilibrium adsorption case applies (7). For the case of chemisorption of two gases A and B on the same surface S we have:

$$A + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} A\text{–}S,$$

$$A\text{–}S \overset{k_2}{\rightarrow} \text{Products},$$

$$B + S \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} B\text{–}S,$$

$$B\text{–}S \overset{k_4}{\rightarrow} \text{Products},$$

$$\theta_{\mathrm{A}} = \frac{K_{\mathrm{A}}P_{\mathrm{A}}}{1 + K_{\mathrm{A}}P_{\mathrm{A}} + K_{\mathrm{B}}P_{\mathrm{B}}},$$

$$\theta_{\mathrm{B}} = \frac{K_{\mathrm{B}}P_{\mathrm{B}}}{1 + K_{\mathrm{B}}P_{\mathrm{B}} + K_{\mathrm{A}}P_{\mathrm{A}}},$$

where $K_{\mathrm{A}} = k_1/k_{-1}$ and $K_{\mathrm{B}} = k_3/k_{-3}$. Since $d(\mathrm{A})/dt = -k_2\theta_{\mathrm{A}}$ and $d(\mathrm{B})/dt = -k_4\theta_{\mathrm{B}}$ for a unimolecular reaction we have:

$$\frac{d(\mathrm{A})}{d(\mathrm{B})} = \frac{k_2\theta_{\mathrm{A}}}{k_4\theta_{\mathrm{B}}} = \frac{K_{\mathrm{A}}k_2P_{\mathrm{A}}}{K_{\mathrm{B}}k_4P_{\mathrm{B}}}.$$

For equal partial pressures and equal adsorption constants $P_{\mathrm{A}} = P_{\mathrm{B}}$ and $K_{\mathrm{A}} = K_{\mathrm{B}}$ so that the relative conversion for A and B becomes

$$d(\mathrm{A})/d(\mathrm{B}) = k_2/k_4.$$

Now suppose adsorption equilibrium is not established because the surface reaction is more rapid than desorption of the reactant. Then it is necessary to assume a steady state concentration of the adsorbed species. This leads to the same form of equations for θ as before (*7*):

$$\theta_{\mathrm{A}}' = \frac{K_{\mathrm{A}}'P_{\mathrm{A}}}{1 + K_{\mathrm{A}}'P_{\mathrm{A}} + K_{\mathrm{B}}'P_{\mathrm{B}}},$$

$$\theta_{\mathrm{B}}' = \frac{K_{\mathrm{B}}'P_{\mathrm{B}}}{1 + K_{\mathrm{B}}'P_{\mathrm{B}} + K_{\mathrm{A}}'P_{\mathrm{A}}},$$

where $K_{\mathrm{A}}' = k_1/(k_{-1} + k_2)$ and $K_{\mathrm{B}}' = k_3/(k_{-3} + k_4)$. Then

$$d(\mathrm{A})/d(\mathrm{B}) = \frac{k_2\theta_{\mathrm{A}}'}{k_4\theta_{\mathrm{B}}'} \qquad \frac{k_2K_{\mathrm{A}}'P_{\mathrm{A}}}{k_4K_{\mathrm{B}}'P_{\mathrm{B}}}$$

and when $k_2 \gg k_{-1}$ and $k_4 \gg k_{-3}$,

$$\frac{d(\mathrm{A})}{d(\mathrm{B})} = \frac{k_2(k_1/k_2)P_{\mathrm{A}}}{k_4(k_3/k_4)P_{\mathrm{B}}}$$

so that for equal partial pressure of reactants $P_{\mathrm{A}} = P_{\mathrm{B}}$ and

$$d(\mathrm{A})/d(\mathrm{B}) = k_1/k_3.$$

Thus, for equal adsorption probability the relative conversion will be unity.

The total conversion will be quite different for the two adsorption schemes. For example, for equal partial pressure of reactants, the total conversion will be $\frac{1}{2}(k_2 + k_4)$ for the equilibrium adsorption case. For the nonequilibrium adsorption case, the total conversion would depend on the rate of the slow reaction and the total conversion would only be twice the slow reaction. The conversions for the nonequilibrium case will be similar to the adsorption equilibrium case when the slower reacting component is strongly adsorbed and the faster reacting component is weakly adsorbed.

Nonequilibrium adsorption explains the observed relative conversion ratio with only the very reasonable assumption of equal adsorption probability. On the other hand, the equilibrium adsorption scheme would require $K_{\mathrm{A}}'k_{\mathrm{A}} = K_{\mathrm{B}}'k_{\mathrm{B}}$; that is, the faster reacting component would have to be adsorbed to a lesser extent than the slower reacting one. It does not seem reasonable that cyclohexane would be adsorbed to a lesser extent than *n*-hexane. Thus it seems certain that adsorption–desorption equilibrium is not established in the competitive conversion of naphthene–paraffin mixtures. In agreement with this, investigators (*2c*) have reported that cyclohexane and *n*-hexane appear to have similar adsorption coefficients.

When mixed with the paraffin cyclohexene, in contrast to cyclohexane, reacts much faster than *n*-octane. This would mean that k_1, the adsorption rate constant, is much larger for cyclohexene than for cyclohexane. It seems reasonable that the olefin should be adsorbed more rapidly since the naphthene and paraffin adsorption requires C–H bond breaking in the chemisorption step.

The results for the present study enable us to conclude that (a) the dehydrocyclization of paraffins is less selective over the Rh– and Pt–catalysts than over the oxide catalysts; or (b) both the naphthene and paraffins undergo conversion to the same extent to nonaromatic products over the oxide catalyst but not the metal catalyst. We favor the first conclusion (a) but more exact data will be required to confirm this.

It appears that the competitive conversions of naphthene and paraffin is dependent on the hydrogen pressure. In view of some recent studies by Parravano (*8*), it is inviting to attribute this dependence to the influence of the hydrogen fugacity on the surface for the reaction:

$$R_3C\text{–}H + 2M \rightleftarrows M\text{–}CR_3 + M\text{–}H \qquad (M = \text{metal surface}).$$

The above reaction would involve hydrogen fugacity in the slow step of the reaction that is required to explain the present results. At the low hydrogen partial pressure for the 1 atm runs the surface hydrogen concentration would be low and may have little influence on the above reaction. But with the higher hydrogen partial pressure at 75 psig, the hydrogen adsorption may increase sufficiently to influence the above equilibrium. If this is the case we would expect the paraffin equilibrium to be much more sensitive to the hydrogen pressure increase than the naphthene as the paraffin–olefin equilibrium would be much more sensitive to hydrogen pressure changes at this temperature than the naphthene–aromatic equilibrium.

The much higher relative conversion of the naphthene at 400° than at 482°C could result in a corresponding change in the adsorption coefficients with temperature. However, deuterium exchange reactions show that paraffins are adsorbed (or at least exchange with deuterium) at temperatures lower than 400°C (*6*). Unfortunately it does not seem possible to obtain a comparison of the adsorption coefficients from the deuterium experiments reported for the paraffin and naphthene. On the other hand, if they do have similar relative adsorption coefficients at both temperatures, then the paraffin must be chemisorbed in a different manner at 482° than at 400° (for example, one change in adsorption could be from homolytic to heterolytic carbon–hydrogen bond fission).

A cycloparaffin has been proposed by some workers as the intermediate in the dehydrocyclization mechanism. The absence of significant amounts of naphthenes in the products was attributed to their much more rapid conversion to aromatics. However, the present study seems to eliminate gas phase naphthenes as an intermediate in the dehydrocyclization mechanism. Adsorbed naphthenes and gas phase cycloolefins can not be eliminated from the dehydrocyclization mechanism by this study. The above conclusion would be altered if diffusion was controlling the selectivity.

Selectivity can also be influenced by diffusion. The selectivity normally changes so that the conversion of the faster reaction is decreased. Wheeler (*9*) classified the conversion of A and B by parallel reactions as Type I selectivity defined by the reaction scheme:

$$A \xrightarrow{k_1} X + Z,$$

$$B \xrightarrow{k_2} Y + Z.$$

If both reactions are first order the selectivity becomes

$$\alpha_A = 1 - (1 - \alpha_B)^S$$

where α_A and α_B are the fraction of A and B reacted and S is the ratio k_A/k_B. For a catalyst of moderate activity with large pores the intrinsic selectivity will be observed. For small pores the selectivity will be decreased but it appears that this decrease of selectivity can proceed no further than the square root relationship

$$S = (k_A D_A / k_B D_B)^{1/2}.$$

Thus for equal diffusion rates D the selectivity can decrease no further than $S = (k_A/k_B)^{1/2}$.

In our case, the diffusion coefficients should be similar since we are comparing very similar reactants, e.g., dimethylcyclohexane and *n*-octane. Hence, even compensating for the pore diffusion, the relative rates of conversion would be greater than naphthene:paraffin = 2:1. Thus pure diffusion can not account for the experimental selectivity being much less than the additive conversions of the pure components for first order reactions. There is evidence that cyclohexane conversion is zero order; if dehydrocyclization is also a zero order reaction the diffusion effects would be similar to that for a first order case.

Diffusion can also influence selectivity by pore mouth poisoning. Here the selectivity can be reduced to the diffusion rates for both reactants; for equal diffusion rates the relative conversion would become 1:1. Thus pore mouth poisoning could be responsible for the observed selectivities. This can not be ruled out by our experiments and will be difficult to establish experimentally. There can be no doubt about poisoning because the activity decreased for all catalysts with time. The important point is how this loss of activity occurs; uniform poisoning would not alter the selectivity from that of pure diffusion but nonuniform pore mouth poisoning could.

There are indications that the selectivity is not completely determined by pore mouth diffusion. To obtain a selectivity of 1:1, then all the naphthene and paraffin diffusing into the pore must be converted. If we compare the selectivity of two naphthenes with the same paraffin (for example cyclohexane and *o*-dimethylcyclohexane with *n*-octane over Pt, Fig. 7) we see that about twice as much *o*-dimethylcyclohexane as cyclohexane was converted. This is the order expected from naphthene reactivity but opposite to that based on diffusion since cyclohexane should diffuse at least as rapidly as *o*-dimethylcyclohexane. Also, cyclohexene conversion, when mixed with *n*-octane, was at least 4–8 times as great as cyclohexane with *n*-octane. Diffusion rates should be similar so the higher conversion of cyclohexene would require it to be converted on the poisoned portion of the pore as well as in the unpoisoned pore. *n*-Octane is converted 2–3 times as rapidly as *n*-hexane over Pt. For the conversion of the *n*-hexane–*n*-octane mixture, the total conversion is 2–3 times lower than for *n*-octane alone but the relative conversion is about 1.5, about the same ratio as calculated from separate conversions with the same naphthene. This is difficult to explain using only diffusion to control selectivity. Thus, until a much more detailed study of the diffusion effects is made, we prefer to ascribe the relative conversion obtained in this study to the simpler explanation of nearly equal adsorption probability with nonequilibrium adsorption.

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