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Reactions of Some C_9 Aromatics on Platinum-Alumina Catalysts

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The reactions of *n*-propylbenzene, ω-methylstyrene, and *o*-ethyltoluene on 0.5% platinum-γ-alumina catalyst were studied in the presence of excess hydrogen using a microreactor pulse technique. Detailed analyses of products were made at five temperatures in the range 337° to 490°C. The reactions of indane were also investigated at 337°, 392°, and 434°C.

Hydrogenation and dehydrogenation were so rapid that equilibrium was attained between olefins and corresponding paraffins at all temperatures. Dehydrocyclization of the substituted benzenes occurred readily to give indane, and subsequent hydrogenolysis of the C_5 ring yielded the isomeric alkylbenzene. These reactions did not attain equilibrium.

Hydrocracking was a relatively minor reaction in comparison with dehydrocyclization and subsequent hydrogenolysis. Toluene was usually the main component of the C_6–C_8 aromatics. Substantial hydrocarbon losses were observed on fresh catalyst and on used catalyst at elevated temperatures.

Changes in catalyst composition, degree of sintering, and poisoning with thiophene showed that dehydrocyclization, hydrogenolysis, and hydrocarbon losses were dependent on the state of the supported metal although equilibrium between paraffins and olefins was still attained. Small amounts of thiophene were found to increase the selectivity of the catalyst for hydrogenolysis.

The mechanisms of these reactions are discussed and the suggestion advanced that multiple π-bonded intermediates play an important part in dehydrocyclization, condensation, and coke formation. Metallic sites which are highly active in this respect are selectively repressed by coke formation, thermal sintering, and chemisorption of thiophene.

INTRODUCTION

Since Moldarskii and co-workers (*1*) reported the formation of naphthalene from *n*-butylbenzene on chromia gel at 475°C, many dehydrocyclization reactions of alkylbenzenes have been investigated using chromia, chromia-alumina, and supported palladium catalysts (*2, 3*). However, little use has been made of low percentage platinum-alumina catalysts, although they have been widely employed for dehydrocyclization of paraffins (*4*). In spite of this considerable body of work little is yet known about the detailed mechanisms of these reactions or the nature of the sites responsible. Studies using alkylbenzenes appear to have several advantages in this respect because alkylation of the aromatic ring is involved and there are many examples of similar reactions in organic or organometallic chemistry, where the mechanisms have been well elucidated. Besides, recent studies on the reactions of substituted benzenes with hydrogen isotopes on metal catalysts (*5, 6*) have provided a fairly clear picture of the nature of the chemisorption of aromatic rings.

The reactions of some C_9 aromatics on platinum-alumina catalysts were chosen for the present study because they have not been investigated in detail on any cata-

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lyst. Herington and Rideal (*7*) reported the formation of ω-methylstyrene and indene from *n*-propylbenzene on chromia-alumina at 475°C, while Kazanskii and co-workers (*8*) have studied the dehydrocyclization of monoalkylbenzenes to indane and its derivatives on 20% platinum-charcoal at 310°C. The formation of indane by dehydrocyclization of *o*-ethyltoluene on mixed oxide catalysts (*9*) and on 0.05 to 1.0% platinum-alumina (*10*) has been reported in the patent literature.

Experimental

Experiments were carried out using the microreactor pulse technique developed by Kokes, Tobin, and Emmett (*11*). The microreactor, shown diagrammatically in Fig. 1, was constructed from mild steel tubing (¼-inch bore, length 8 inches) and had brass couplings brazed at both ends. One of the couplings carried a coaxial thermocouple well made from stainless steel tubing ($\frac{1}{32}$-inch bore). Two injection ports of O.B.A. studding ($\frac{1}{16}$-inch bore, length 2 inches) were brazed onto the central tube at inlet and outlet ends, respectively. The reactor was enclosed in a tightly fitted aluminium jacket (½-inch thick) and wound with a mica-insulated heating coil which was adjusted to give isothermal heating. The whole assembly was thermally insulated with asbestos lagging. Temperatures were measured by means of an iron-constantan thermocouple and were found to remain constant to ±3°C at 480°C over a period of 8 hr.

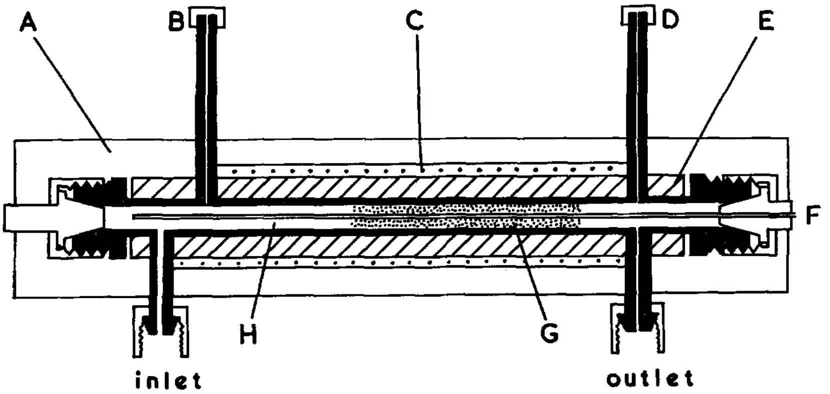

FIG. 1. Diagrammatic cross section of the microreactor. A, asbestos lagging; B, first injection port; C, mica-insulated heater; D, calibration port; E, aluminium sheath; F, thermocouple well; G, catalyst bed; and H, quartz wool packing.

The microreactor was fitted into the flow line of a GLC apparatus using hydrogen as carrier gas and a katharometer for detection. The column, katharometer, and carrier gas preheater were housed in an electrically heated oven and connections between the microreactor, column, and katharometer were of $\frac{1}{16}$-inch bore copper tubing in order to reduce dead volumes to a minimum. For the same reason the microreactor was mounted on the oven lid directly above the column ends and the katharometer.

In standard experiments, after catalyst pretreatment, thirteen pulses of reactant, each 5 μl in volume, were injected through a serum cap on the first port at intervals of 30 min. A microliter syringe with a Chaney Adaption was used for injection. The reproducibility of the injection method was tested using the calibration port and it was found that sample size did not vary by more than 1%.

The reaction products were separated on a 12-ft column consisting of two equal sections, in series, of 20% w/w Apiezon L and Polyphenylether (Monsanto Chem. Comp.), respectively, dispersed on Celite (85–100 mesh B.S.S.) packed in copper tubing ($\frac{3}{16}$-inch ID). The column was operated at 164°C and a flow rate of 34 ml/min at STP with a pressure of approximately 1 atm at the reactor inlet. The detector gave a linear response to sample size, and sensitivity coefficients for individual hydrocarbons were evaluated and frequently checked. Hydrocarbon gases in the C_1–C_3 range were eluted as one peak and quantitative analysis was not attempted. There was also considerable overlap of the peaks corresponding to isopropylbenzene and *o*-xylene but the resolution was sufficient to show that yields of *o*-xylene from *n*-propylbenzene or ω-methylstyrene and of isopropylbenzene from *o*-ethyltoluene or indane could be neglected. Allylbenzene and *n*-propylbenzene had exactly the same retention volumes but the amount of the former compound expected to be present if it were in equilibrium with ω-methylstyrene, was so small that it was ignored.

MATERIALS

All catalysts were supplied by I.C.I. (Billingham Division) and, with the exception of 0.9% platinum-silica, were in the form of ⅛ × ⅛ inch cylindrical pellets. Platinum-alumina catalysts were of two types. Type "A" consisted of preformed alumina pellets impregnated with platinum chloride solution to give the required platinum content. The pellets were dried at 120°C and then reduced in hydrogen at 250°C.

In the preparation of type B a wet filter cake of alumina was slurried with the required amount of platinum chloride solution which had been saturated with hydrogen sulfide. The slurry was dried at 120°C, pelleted with graphite, and calcined at 500°C for 6 hr. This catalyst was of the "co-gelled" type.

Platinum-alumina catalysts used were:

0.5% platinum-γ-alumina, B
0.5% platinum-γ-alumina, A
0.3% platinum-γ-alumina, A_1
0.5% platinum-α-alumina, A_2

The 0.9% platinum-silica was supplied in granules 8 mesh B.S.S. The γ-alumina and α-alumina had surface areas of approximately 80 and 30 m^2/g, respectively.

A fresh sample of catalyst (60–100 mesh B.S.S.) was used for each series of thirteen injections. The volume of the catalyst was the same in every experiment and, in the case of A (0.5% platinum-γ-alumina), which was generally employed unless otherwise stated, this corresponded to 1.333 g.

The standard pretreatment of the catalyst was to sweep it with hydrogen for 2½ hr at room temperature followed by heating over a period of 50 min to reaction temperature. The catalyst was maintained at this temperature for a further 40 min before injecting the first pulse of reactant.

Hydrogen (B.O.C.) was passed through magnesium perchlorate to remove water and through a bed of 0.9% platinum-silica at 300°C to remove oxygen. Further elimination of water and other condensables was effected by means of activated molecular sieves (Linde 5A) backed by a trap at −195°C.

n-Propylbenzene (Eastman Kodak Co.) and *o*-ethyltoluene, dried over magnesium perchlorate, were found to be pure by GLC analysis.

ω-Methylstyrene (Aldrich Chemical Co. Inc.) and indane (B.D.H.) were purified by preparative GLC as were other compounds used for calibration purposes.

Thiophene (B.D.H.) was also purified by preparative GLC and mass spectrometric analysis showed it to be greater than 99.5% pure.

RESULTS

The concentrations of the individual aromatic products are expressed as percentages of the number of g moles of reactant. From these values the total recovery of aromatic material (T.R.) and the yield of transformed hydrocarbon (T.H.) were calculated. The latter refers to products arising from reactions other than hydrogenation or dehydrogenation of the initial reactant.

All the reactants gave the same general trends in product distribution as a function of the number of pulses injected, with every sample of catalyst. These trends are illustrated by the data given in Table 1,

TABLE 1

SELECTED PRODUCT DISTRIBUTIONS FROM REACTION OF *n*-PROPYLBENZENE ON CATALYST A AT 479°C

	Pulse no.					
	1	2	3	4	8	12
Benzene	2.8	1.2	1.2	1.0	1.2	0.9
Toluene	4.9	3.9	3.1	3.6	3.6	3.0
Ethylbenzene	3.4	3.6	2.8	3.5	3.2	3.1
Isopropylbenzene	1.8	1.7	1.5	1.9	1.7	1.7
n-Propylbenzene	7.5	20.2	23.1	23.6	26.5	28.8
o-Ethyltoluene	1.3	1.4	1.5	1.3	1.3	1.5
α-Methylstyrene	0.8	1.4	1.7	1.9	2.2	2.2
ω-Methylstyrene	0.7	2.1	2.3	2.9	3.1	3.3
Indane	8.0	11.5	11.8	10.9	11.3	11.8
Indene	17.0	25.3	26.1	26.0	26.9	27.0
T.H.	40.0	50.0	49.7	50.1	51.4	51.2
T.R.	48.2	72.3	75.1	76.6	81.0	83.3

which shows selected product distributions for the reaction of *n*-propylbenzene at 479°C. There was a continuous increase in the total recovery of aromatic material with pulse number, although the major changes took place over the first three pulses. The yields of transformed hydrocarbon and unreacted *n*-propylbenzene also increased in a similar fashion while the corresponding yields of the C_6–C_8 compounds and of the C_1–C_3 gases decreased. After the first three pulses the product distributions showed a slight increase only in *n*-propylbenzene and ω-methylstyrene percentages and the yields of other compounds remained constant or decreased slightly. While there were minor variations in these trends with pulse number from one reactant to another the same general behavior was noted for all the compounds studied at different temperatures. The average product distribution from pulses 4 to 13 inclusive was therefore taken as being representative of reaction at a particular temperature.

Average product distributions for the reaction of *n*-propylbenzene at five temperatures in the range 334–479°C are shown in Table 2. The yield of transformed hydrocarbon was almost doubled in this temperature range and there was a corresponding decrease of some 10% in the amount of aromatic material recovered. At 334°C *o*-ethyltoluene and indane were important products. However, as the temperature increased the yield of *o*-ethyl-

TABLE 2

AVERAGE PRODUCT DISTRIBUTIONS FROM REACTION OF *n*-PROPYLBENZENE ON CATALYST A

	°C				
	334°	366°	392°	434°	479°
Benzene	1.4	1.1	0.9	1.0	1.0
Toluene	4.2	4.0	3.6	3.0	3.4
Ethylbenzene	1.5	1.8	1.9	2.6	3.4
Isopropylbenzene	0.8	1.1	1.4	1.7	1.6
n-Propylbenzene	63.5	61.0	56.8	37.3	26.9
o-Ethyltoluene	11.3	9.0	5.8	3.0	1.2
α-Methylstyrene	—	—	—	0.9	1.9
ω-Methylstyrene	—	—	—	1.7	3.2
Indane	8.3	11.5	14.6	17.6	11.1
Indene	—	1.2	3.2	15.8	26.2
T.H.	27.5	29.7	31.4	45.6	49.8
T.R.	91.0	90.7	88.2	84.6	79.9

toluene fell away sharply but there was a continuous increase in the yield of indane and indene. Olefinic products also became important at the higher temperatures. Toluene accounted for more than one-half of the C_6–C_8 fraction at lower temperatures, but ethylbenzene was formed in comparable quantities in the higher end of the temperature range.

TABLE 3

Average Product Distributions from Reaction of *o*-Ethyltoluene on Catalyst A

	°C 340	375	392	424	488
Benzene	0.1	0.2	—	—	0.4
Toluene	1.1	1.3	1.0	0.7	2.1
Ethylbenzene	0.5	0.5	0.5	0.3	0.9
o-Xylene	0.8	1.0	0.9	0.7	1.1
n-Propylbenzene	3.7	3.5	2.7	1.5	1.0
o-Ethyltoluene	74.2	72.1	62.9	65.3	50.5
o-Vinyltoluene	—	—	—	0.9	2.2
Indane	19.4	24.0	25.8	20.7	11.4
Indene	—	0.4	2.6	12.1	27.7
T.H.	25.6	30.9	33.5	36.0	44.6
T.R.	99.8	103.0	96.4	102.2	97.3

The reactions of ω-methylstyrene were studied in the same temperature range. The same products were obtained as from *n*-propylbenzene and variations in their yields were very similar; the only difference was slightly greater loss of hydrocarbon at higher temperatures.

As *o*-ethyltoluene was an important product from both *n*-propylbenzene and ω-methylstyrene its reactions were also studied. Some average product distributions, given in Table 3, show that indane and indene were the major products and that the yield of the former was somewhat higher than from the previous reactants at lower temperatures. At the same time lower yields of C_6–C_8 products showed that hydrocracking of the side chains occurred to a lesser extent. Again there was a continuous increase in the yield of transformed hydrocarbon but little loss of aromatic material occurred.

Broad unresolved ESR signals were obtained from catalyst samples which were used for the reactions of *n*-propylbenzene or *o*-ethyltoluene at 479° and 488°C, respectively.

The reactions of indane were also investigated and average product distributions for three temperatures are shown in Table 4. Both the yield of products due to transformation reactions and the total recovery of material decreased as the temperature was raised. In this case, however, there was a considerable fall in the fraction which the transformed hydrocarbon made of the total recovered. This was due mainly to a very sharp fall off in the yield of *o*-ethyltoluene which accounted for some 80% of transformed hydrocarbon at 337°C. The yields of C_6–C_8 products were also lower than those from the other reactants and their distributions resembled those from *o*-ethyltoluene more closely than from *n*-propylbenzene.

TABLE 4

Average Product Distributions from the Reaction of Indane on Catalyst A

	°C		
	337	392	434
Benzene	0.5	0.3	1.0
Toluene	0.9	0.5	1.1
Ethylbenzene	0.4	0.5	0.8
o-Xylene	0.5	0.5	0.8
n-Propylbenzene	4.2	2.3	1.9
o-Ethyltoluene	28.1	8.6	4.8
Indane	57.0	61.5	35.8
Indene	1.9	20.0	29.6
T.H.	34.6	12.7	10.4
T.R.	93.5	94.2	75.8

The influence of pretreatment on the activity of the catalyst for the reaction of ω-methylstyrene was tested in the following manner. Catalyst samples were raised to 480°C and maintained at that temperature for the usual period (40 min), followed by rapid cooling to the required reaction temperature. The first pulse of reactant was injected when 30 min had elapsed after treatment at 480°C had been stopped. Product distributions obtained from the initial pulse of reactions at 339°, 390°, and 431°C are given in Table 5 together with corresponding distributions obtained using catalyst which had been subject to the normal pretreatment. The more drastic thermal treatment resulted in a higher total recovery and a lower yield of transformed products, especially at the lowest temperature. On the other hand the extent of hydrogenation of ω-methylstyrene to *n*-propylbenzene was unaltered. Subsequent product distributions showed the same general trends observed with catalyst which had received standard pretreatment but the changes were much less marked over the first three doses.

Some catalyst samples were subject to more prolonged heat treatment at 480°C before carrying out reaction of ω-methylstyrene at that temperature. The initial and average product distributions, corresponding to various periods of pretreatment, are given in Table 6. The major effect of sintering the catalyst in this manner was the recovery of a larger quantity of hydrocarbon with the same carbon skeleton as that of ω-methylstyrene and higher yields of indane and indene from the initial pulses.

The reactions of *n*-propylbenzene and *o*-ethyltoluene on catalyst B were investigated in the temperature range 322° to 490°C and an approximate activation energy of 19 kcal/mole obtained for hydrocarbon loss from both reactants. Although the products were the same as those obtained using catalyst A, lower yields of transformed hydrocarbon were obtained. On the other hand B was more active than A catalyst which had been pretreated to 480°C before cooling to reaction temperature.

TABLE 5

Initial Product Distributions from Reaction of ω-Methylstyrene on "Sintered" and Normal Catalyst A

	°C					
	339[a]	336[b]	390[a]	390[b]	437[a]	431[b]
Benzene	1.0	1.5	1.4	1.6	1.9	1.9
Toluene	0.9	4.8	2.4	4.1	3.3	4.3
Ethylbenzene	2.5	1.8	1.0	2.8	1.5	3.0
Isopropylbenzene	0.2	0.8	1.0	1.4	1.7	2.1
n-Propylbenzene	89.0	57.2	57.2	45.6	30.0	18.9
o-Ethyltoluene	1.2	12.1	3.3	3.8	2.5	2.3
α-Methylstyrene	—	—	—	—	1.2	0.3
ω-Methylstyrene	—	—	0.7	0.9	3.8	1.4
Indane	5.1	12.3	12.2	16.2	10.5	11.8
Indene	—	—	2.7	6.3	8.4	10.0
T.H.	10.9	33.3	24.0	36.2	31.0	35.7
T.R.	99.9	90.5	81.9	82.7	63.8	56.0

[a] Catalyst heated to 480°C before reaction.

[b] Catalyst pretreated in the normal manner.

The influence of varying the catalyst support was also tested by studying the reaction of *n*-propylbenzene at 390°C on 0.5% platinum-α-alumina and the reaction of ω-methylstyrene on 0.9% platinum-silica at 386°C. While the total hydrocarbon recovered was much the same in these reactions as when using platinum-γ-alumina, the yield of transformed hydrocarbon was reduced by a factor of three in both cases.

The relative proportions of the products remained essentially the same, indane being the main product and toluene the most important component of the C_6–C_8 fraction. The main difference was a decrease in the ratio of *o*-ethyltoluene to indane.

The effect of varying the platinum content of the catalyst on the reaction of ω-methylstyrene at 390°C was tested using 0.3% platinum-γ-alumina. While the total recovery of aromatic compounds did not differ significantly from that obtained using the standard catalyst, the yield of transformed product fell from 39 to 31%. Reduced yields of indane and indene accounted for most of this decrease and although the total amount of C_6–C_8 products remained the same benzene was the most important component in this case.

The catalytic activity of the γ-alumina support for these reactions was also tested after it had received the standard pretreatment. The only products from *n*-propylbenzene and *o*-ethyltoluene at 480°C were trace amounts of corresponding olefins and C_6–C_8 compounds. Reaction of ω-methylstyrene at the same temperature gave slightly greater yields of C_6–C_8 compounds together with some isomerization to α-methylstyrene and allylbenzene, but the ratio of α-methylstyrene to the initial olefin was well removed from the equilibrium value. Very little reaction of indane and indene took place on γ-alumina at 392°C, the only detectable products being benzene and toluene. In all these experiments benzene was the main component of the C_6–C_8 fraction and hydrocarbon losses were much lower than with supported metal catalysts.

TABLE 6

PRODUCT DISTRIBUTIONS FROM REACTIONS OF ω-METHYLSTYRENE AT 480°C ON CATALYST SAMPLES WHICH RECEIVED VARIED HEAT TREATMENT

	Initial			Average		
	a	*b*	*c*	*a*	*b*	*c*
Benzene	1.3	2.4	1.9	0.8	1.2	0.8
Toluene	2.6	4.3	2.9	2.6	3.1	1.8
Ethylbenzene	1.6	2.8	2.5	2.2	3.3	1.9
Isopropylbenzene	0.8	1.5	0.7	1.2	1.5	1.2
n-Propylbenzene	6.4	6.9	18.9	21.8	23.8	30.2
o-Ethyltoluene	0.8	0.9	0.9	0.8	0.2	0.2
α-Methylstyrene	0.2	0.7	1.2	1.8	3.0	4.8
ω-Methylstyrene	0.8	0.9	3.4	5.1	7.6	14.4
Indane	4.8	6.3	7.8	7.1	7.3	5.2
Indene	8.7	13.6	16.3	17.2	22.0	18.5
T.H.	20.8	32.5	34.2	33.7	41.6	34.4
T.R.	28.0	40.3	56.5	60.6	73.0	79.0

[a] Normal heat treatment.

[b] Normal heat treatment + 2 1/2 hr at 480°C.

[c] Normal heat treatment + 96 hr at 480°C.

The poisoning effect of thiophene on the activity of 0.5% platinum-γ-alumina for the conversion of ω-methylstyrene at 388°C was tested in two ways. In the first series of experiments the hydrocarbon contained 1% by volume of thiophene and in the second the catalyst had been subjected to a 6 μl pulse of thiophene 2 min prior to the injection of the first pulse. The presence of thiophene had very little apparent effect on the hydrogenation–dehydrogenation activity of the catalyst and unconverted ω-methylstyrene was returned mainly as *n*-propylbenzene as in the normal experiments. The yields of transformed hydrocarbon from these experiments and from the corresponding normal experiments are plotted as a function of pulse number in Fig. 2a. The yields from thiophene-containing reactant decreased from 36 to 10% and remained fairly constant thereafter. The normal series of reactions showed an increase from 36 to 42% over the first few pulses followed by a slow decrease. On the other hand, reaction on prepoisoned catalyst gave an initial yield of 9% followed by a slow increase to a fairly constant value of 17%. Purging with hydrogen at reaction temperature for 18 hr brought the yield up to 24%. Individual yields of *o*-ethyltoluene are shown in Fig. 2b and those of indane and toluene in Fig. 2c. The yield of *o*-ethyltoluene from ω-methylstyrene with added thiophene was initially double that from pure ω-methylstyrene but decreased rapidly with pulse number to a very low value while the percentages from prepoisoned catalyst increased gradually. The yield of indane, using both methods of poisoning, was always less than that from normal reactions and fell off rapidly from 15 to 7% in the reactions of poisoned reactant. The initial pulse on prepoisoned catalyst also gave a yield of 7% followed by a gradual rise to a constant value of 11%. Yields of toluene also showed similar trends to those of indane. Purging the prepoisoned catalyst with hydrogen for 18 hr increased the yields of all three products.

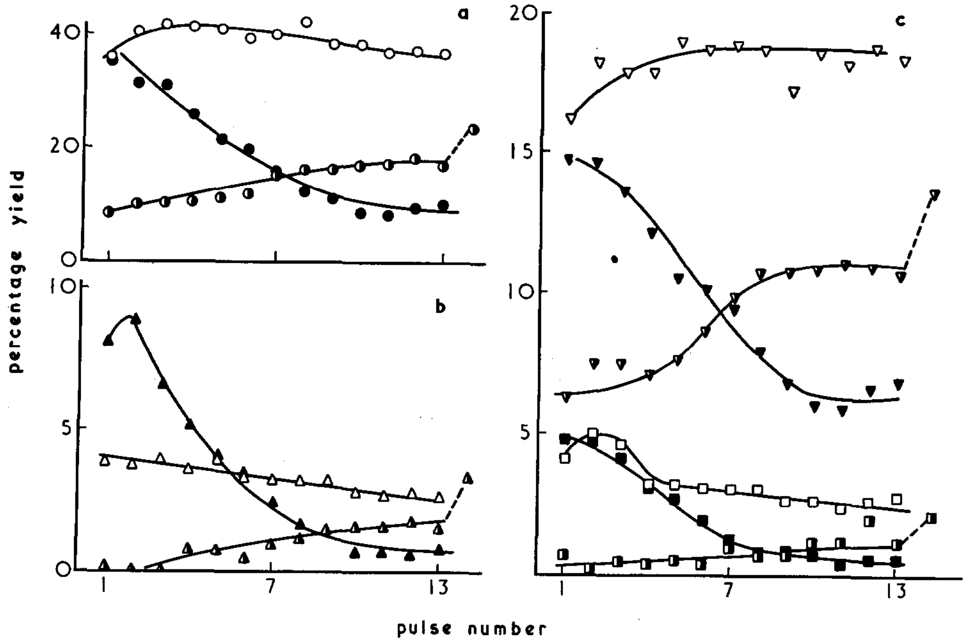

FIG. 2. Product yields from the reaction of ω-methylstyrene at 388°C in normal reactions (open symbols); with 1% thiophene added (blocked symbols); and on prepoisoned catalyst (half-blocked symbols). (a) ○, T.H.; (b) △, *o*-ethyltoluene; (c) ▽, indane; and □, toluene. The broken line signifies 18 hr purging with hydrogen.

Since the presence of a small amount of thiophene had a beneficial effect on the formation of *o*-ethyltoluene and a detrimental effect on the formation of indane from ω-methylstyrene, the reaction of indane containing 1% by volume of thiophene was also tested at 388°C. The yields of *o*-ethyltoluene and *n*-propylbenzene, together with those obtained from the normal reaction of indane, are plotted against pulse number in Fig. 3. Initially the concentrations of these products were somewhat higher in the presence of thiophene than in its absence, although they decreased rapidly to low values. In this experiment purging with hydrogen for 18 hr followed by reaction of pure indane resulted once again in increased yields of products.

The presence of thiophene on the catalyst also reduced hydrocarbon losses. While the initial pulses of pure ω-methylstyrene and indane showed losses of 17 and 24%, respectively, these values were reduced to 13 and 9% when thiophene was present in both reactants. There was no loss of hydrocarbon from the initial pulse of ω-methylstyrene on prepoisoned catalyst although a loss of 6% was recorded from the pulse injected after 18 hr of hydrogen purging.

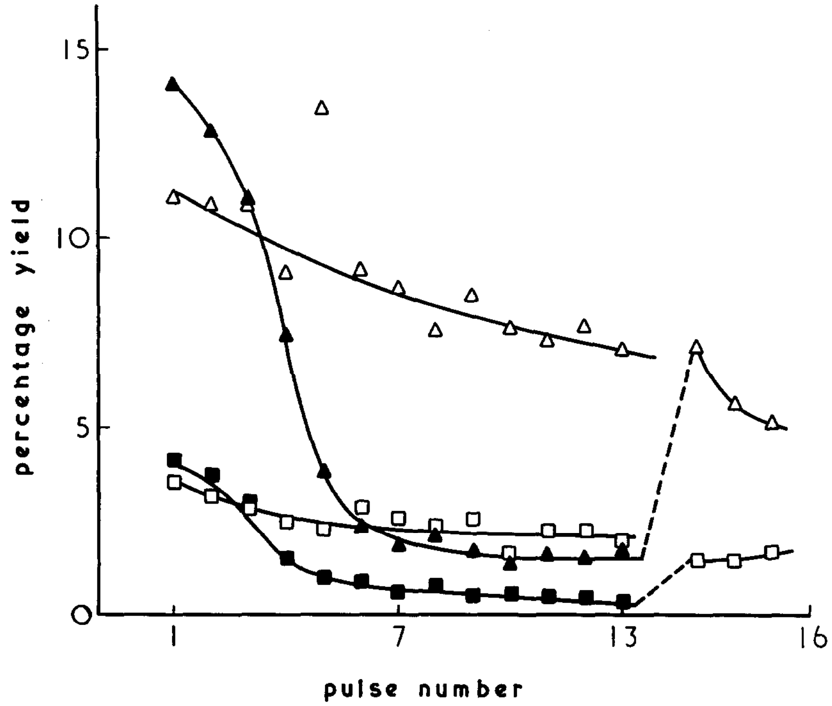

FIG. 3. Product yields from the reaction of indane in normal reactions (open symbols) and with 1% thiophene added (blocked symbols); triangles, *o*-ethyltoluene; and squares, *n*-propylbenzene. Open symbols after broken line are yields from reaction of pure indane after 18-hr purging with hydrogen.

A partially resolved peak in the chromatograms, corresponding to a C_4 compound, was observed when the reactants contained thiophene. This showed that thiophene decomposition was taking place and the extent of this reaction decreased with pulse number in the same manner as the conversion of C_9 hydrocarbons.

DISCUSSION

Although the results present a complex picture of parallel, reversible, irreversible and consecutive reactions these can be conveniently divided into four groups: hydrogenation and dehydrogenation, interconversion of C_9 hydrocarbons, degradation of C_9 aromatics to C_6–C_8 alkylbenzenes and reactions resulting in nonrecovery of the total input of benzene rings.

Hydrogenation and dehydrogenation in the side groups occurred rapidly. Assuming that the partial pressure of hydrogen remained constant for every reactant over the temperature range employed, it is possible to ascertain whether the following reactions were in equilibrium:

$$\text{indane} \rightleftharpoons \text{indene} + H_2 \quad (1)$$

$$\text{isopropylbenzene} \rightleftharpoons \alpha\text{-methylstyrene} + H_2 \quad (2)$$

$$n\text{-propylbenzene} \rightleftharpoons \omega\text{-methylstyrene} + H_2 \quad (3)$$

$$o\text{-ethyltoluene} \rightleftharpoons o\text{-vinyltoluene} + H_2 \quad (4)$$

Plots of $\log_{10}(C_9H_n/C_9H_{n+2})$ against $1/T°K$ for each of these reactions are shown in Fig. 4. In spite of the fact that the hydrogen pressure varies to some extent because of varying degrees of reaction and changes in the character of the reactant, whether olefinic or paraffinic, fairly linear relationships were obtained. Approximate $\Delta H°$ values of 25, 23, 27, and 25 kcal/mole

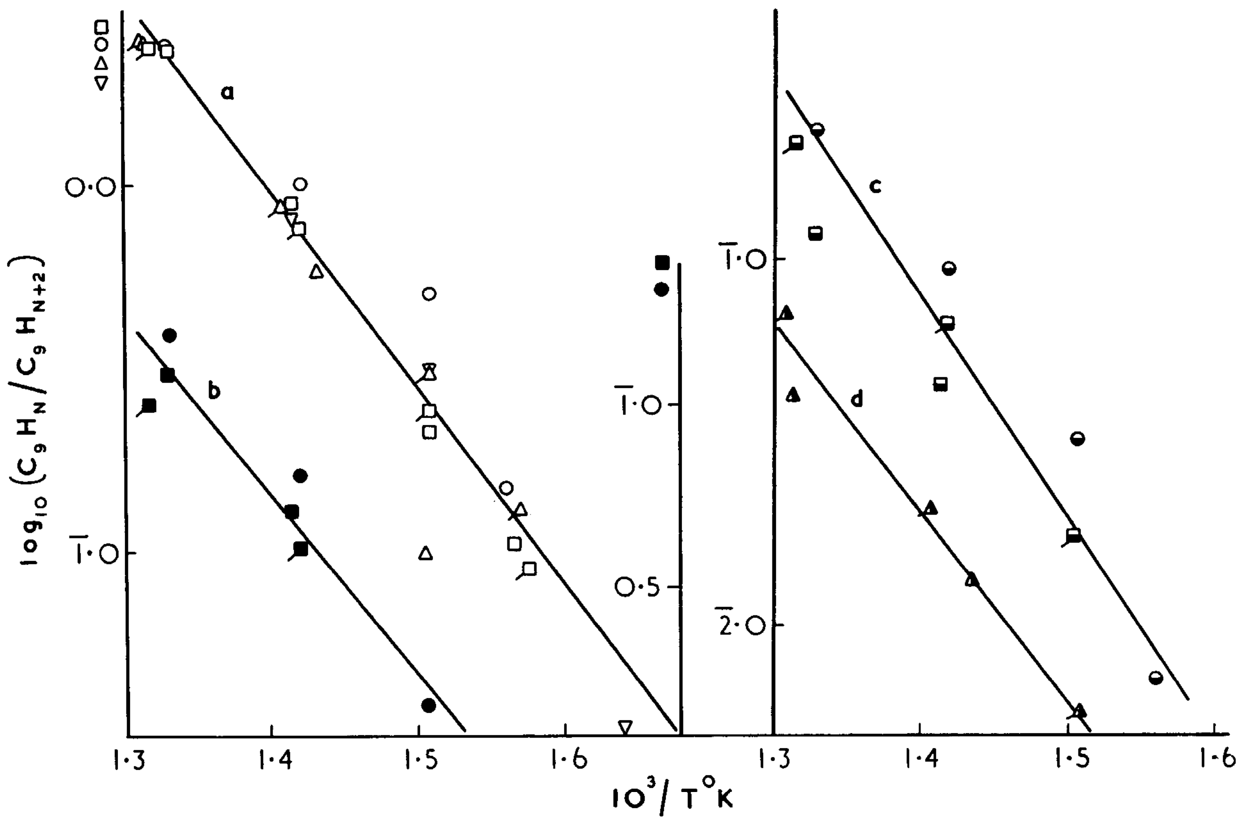

FIG. 4. Temperature dependence of ratios of various olefins to corresponding paraffins [a, reaction (1); b, reaction (2); c, reaction (3); d, reaction (4); see text]. Reactants—square symbols, *n*-propylbenzene; circles, ω-methylstyrene; triangles, *o*-ethyltoluene; and inverted triangles, indane. Tailed symbols—reactions on B catalyst.

for reactions (1–4), respectively, were estimated from the gradients of the lines and found to be in fair agreement with the corresponding values of 24, 27, 28, and 29 kcal/mole, at 480°C, calculated from the appropriate thermodynamic data available in the literature (*12–15*). Thermal sintering of the catalyst, reduction in the percentage of platinum, change of the support, or poisoning with thiophene did not result in any serious departure from equilibria in these reactions.

The formation of indane and *o*-ethyltoluene from *n*-propylbenzene and ω-methylstyrene, of indane and *n*-propylbenzene from *o*-ethyltoluene, and of both alkylbenzenes from indane shows that dehydrocyclization and hydrogenolysis occur simultaneously. These reactions are represented by the following equations:

$$n\text{-propylbenzene} \rightleftharpoons o\text{-ethyltoluene} \quad (5)$$

$$o\text{-ethyltoluene} \rightleftharpoons \text{indane} + H_2 \quad (6)$$

$$n\text{-propylbenzene} \rightleftharpoons \text{indane} + H_2 \quad (7)$$

We believe that the bicyclic compound is an essential intermediate in isomerizing *n*-propylbenzene to *o*-ethyltoluene. This conclusion is supported by an examination of various ratios of products and reactants at different temperatures.

If indane is an intermediate in isomerization than reactions (6) and (7) should approach equilibrium more closely than reaction (5). The average values of $\log_{10}$ (*o*-ethyltoluene/*n*-propylbenzene) obtained from each reactant are plotted against $1/T$°K in Fig. 5a. Only indane gave ratios which approximate closely to the corresponding equilibrium ratios calculated from thermodynamic data (*14*). The ratios from *n*-propylbenzene and ω-methylstyrene are much lower and those from *o*-ethyltoluene much higher than the equilibrium values.

Similar ratios corresponding to reactions (6) and (7) are plotted against $1/T$°K in Fig. 5b and c. Values of $\log_{10}$ (indane/*o*-ethyltoluene) obtained from indane only slightly exceeded those from *n*-propylbenzene and ω-methylstyrene as would be expected if indane were an intermediate in the isomerization of *n*-propylbenzene to *o*-ethyltoluene. On the other hand the values for *o*-ethyltoluene were much lower. The plots in Fig. 5c show the same features. Values of $\log_{10}$ (indane/*n*-propylbenzene) lie in the same region when indane and *o*-ethyltoluene are the reactants, but are well above those from *n*-propylbenzene and ω-methylstyrene. While the true equilibrium ratios cannot be ascertained for reactions (6) and (7) because of the uncertainty in hydrogen pressure, it is obvious that approach to equilibrium is closer in (6) and (7) than in (5), which supports the idea that isomerization occurs via formation and hydrogenolysis of indane. The increasing thermodynamic stabilities of bicyclic compounds, relative to other C_9 aromatics, is also reflected by the results. Thus the conversion of indane to C_9 alkylbenzenes decreased with increasing temperature while conversion of each alkylbenzene to indane and indene increased, and at the same time the yield of isomeric C_9 product decreased. The apparent divergence from, rather than a closer approach to, equilibrium in these reactions at higher temperatures (Fig. 5a) is probably due to greatly reduced activity of the catalyst as a consequence of thermal sintering and more drastic poisoning by carbonaceous deposits. This is borne out by the fact that similar ratios, obtained using catalyst B which had already been well sintered during preparation, approached their equilibrium values more closely for reaction (5) at higher temperatures. Furthermore the yield of C_6–C_8 compounds showed little or no increase with temperature on catalysts of type A and this is best attributed to reduced activity.

The inactivity of γ-alumina for catalyzing ring formation or ring cleavage implies that these reactions take place on the metal. Moreover, similar reactions were observed on platinum-silica and have been reported on platinum-charcoal catalysts (*8*). We believe that this sequence of reactions on the metal provides an alternative mechanism, for some carbon-skeleton isomerizations on dual-function catalysts, to the usually accepted mechanism which re-

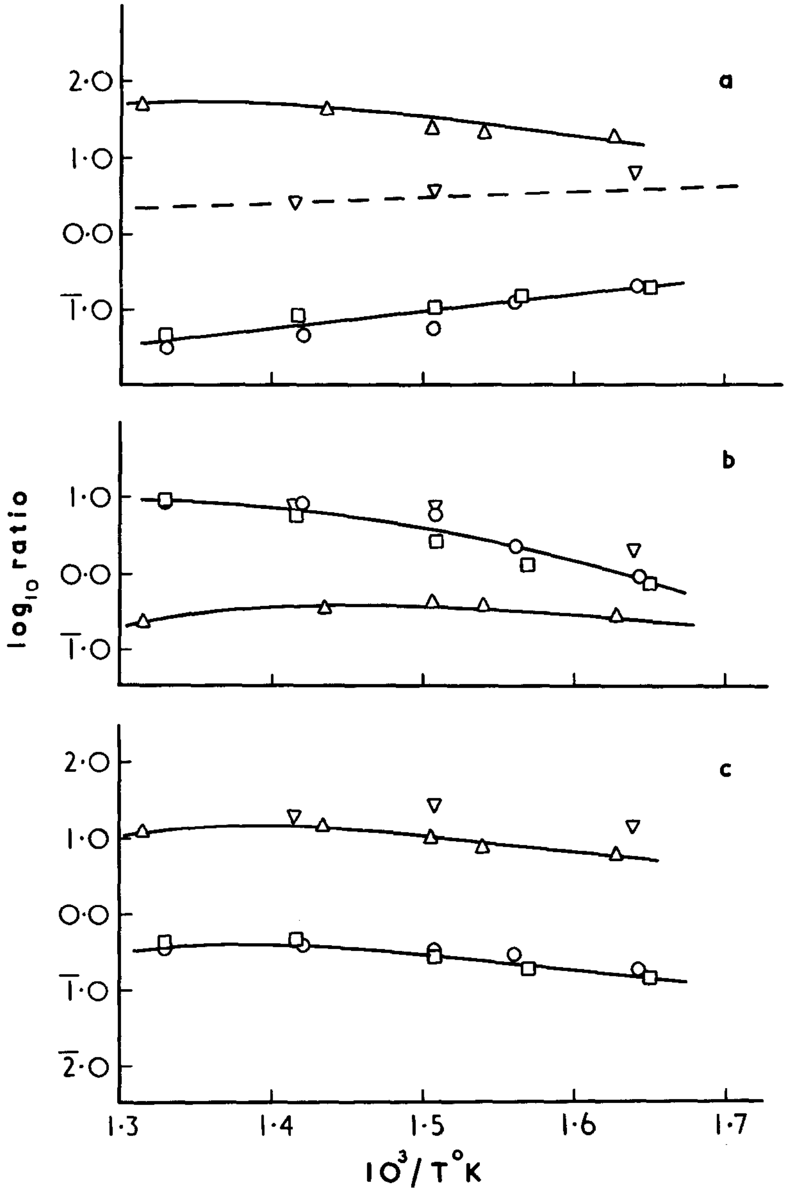

FIG. 5. Temperature dependence of ratios of various C_9 compounds [a, reaction (5); b, reaction (6); c, reaction (7); see text]. Reactants—□, *n*-propylbenzene; ○, ω-methylstyrene; △, *o*-ethyltoluene; and ▽, indane. The broken line in (a) shows the calculated thermodynamic equilibrium values.

quires migration of intermediate products to acidic sites of the support and subsequent rearrangement via carbonium ion mechanisms. This conclusion agrees with that of Gault and co-workers (*16*) who observed that interconversion of *n*-hexane, 2-methylpentane, and 3-methylpentane on low percentage platinum-alumina catalysts takes place through formation of methylcyclopentane followed by hydrogenolysis on metallic sites.

Although the precise nature of the mechanism of dehydrocyclization on platinum-alumina is unknown some results obtained in related fields of study may be relevant. Recent work on exchange of cycloalkanes (*17, 18*) and alkylbenzenes (*5*) with deuterium on metal films, supports the concept that π-bonded intermediates participate in many reactions of hydrocarbons on transition metals. So far these ideas have been applied mainly to those reactions which involve splitting and reforming of carbon-hydrogen bonds. There seems to be no reason why similar intermediates should not participate at higher temperatures in carbon–carbon bond rupture and formation. Current developments in organometallic chemistry support this view. Wilke (*19*) has described dehydrocyclization reactions which involve π-bonded complexes of C_{12} hydrocarbons with nickel. Fisher (*20*) has reviewed several alkylation reactions of cycloheptatrienyl metal carbonyls and quotes some examples where ring contraction in the cyclic ligand also occurs.

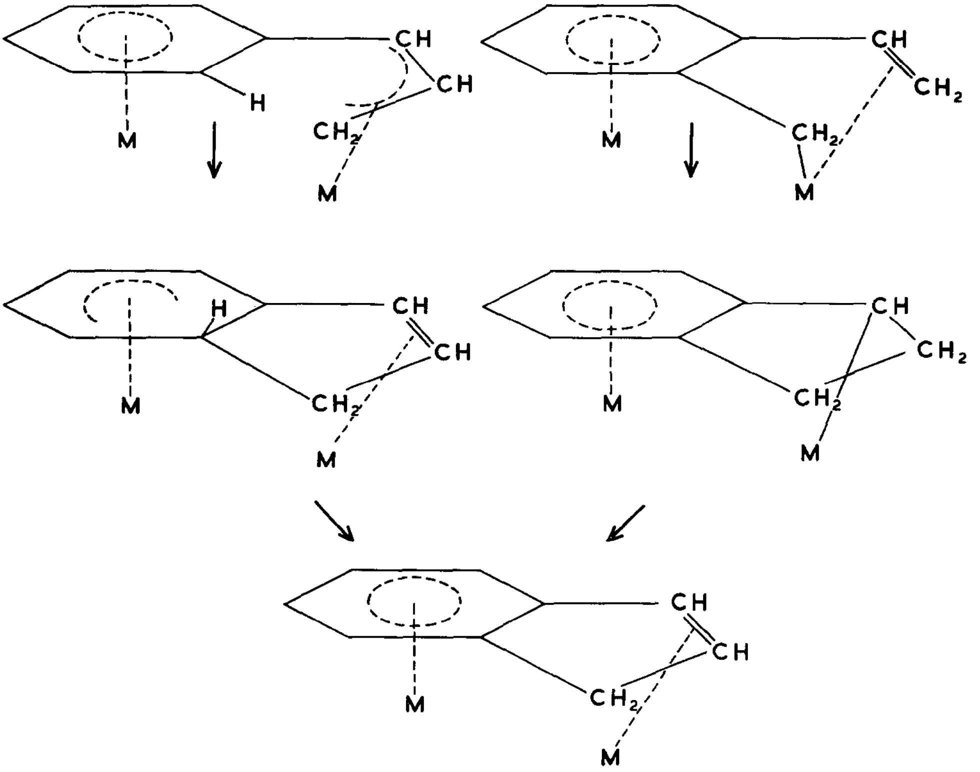

Fig. 6. Possible intermediates in ring closure.

The exchange of alkylbenzenes with deuterium on nickel films has provided good evidence for the simultaneous adsorption of the benzene ring as a π complex and dissociative interaction of the side groups with adjacent active centers. Similar bonding of aromatics to platinum atoms in reforming catalysts has been suggested (*21*). Thus all carbon atoms in the side groups of the C_9 reactants may be involved in bonding to the metal surface in addition to chemisorption through the aromatic ring. Possible intermediates which participate in dehydrocyclization are shown in Fig. 6.

The much lower activity of α-alumina or silica-supported platinum may be mainly a consequence of the reduced surface area of the support, although variations in the electronic properties of the catalyst, similar to those found by Nicolescu (*22*), may be important.

Hydrocracking of C_9 reactants to C_6–C_8

alkylbenzenes was a relatively minor reaction and did not account for more than 25% of the transformed hydrocarbon from *n*-propylbenzene or ω-methylstyrene. The lower yields, of less than 10%, obtained from indane and *o*-ethyltoluene indicate that a C_3 side group is more prone to attack than ethyl or methyl substituents. The preferential formation of toluene from indane and *o*-ethyltoluene suggests that ethyl is more easily removed than a methyl group, while the resistance of an adsorbed benzyl species to further rupture may also explain the preferential formation of toluene from *n*-propylbenzene and ω-methylstyrene. The high yields of *o*-ethyltoluene from indane suggest that the bonds between the least-substituted carbon atoms are more readily broken, especially at lower temperatures. The hydrogenolysis of substituted cyclopentanes on supported platinum catalysts shows similar behavior (*23, 24*).

The isomerization of the C_3 side groups in *n*-propylbenzene and ω-methylstyrene to give the corresponding *iso* compounds was unaffected by sintering of the catalyst in contrast with the effect on dehydrocyclization and hydrogenolysis. The support probably plays an important role in this isomerization in agreement with the observation that extensive methyl shift took place in the side group when ω-methylstyrene was passed over γ-alumina.

The substantial loss of carbon on fresh catalyst and at elevated temperatures on used catalyst must be associated mainly with reactions on the metal. This is shown by the influence of sintering, poisoning with thiophene, and the greatly reduced loss in the reactions of ω-methylstyrene on alumina itself. The activation energy of 19 kcal/mole for the loss of alkylbenzenes on B catalyst agrees well with the value of 18.2 kcal/mole found for the loss of benzene on reforming catalysts in the presence of hydrogen over a similar temperature range (*21*). There are two possible sources of loss, either extensive rupture of the aromatic ring and side groups to give gaseous paraffins, or condensation to larger molecules not detectable by the GLC technique, together with formation of hydrogen-deficient residues, known collectively as coke. The first mode of loss is undoubtedly partly responsible because the C_1–C_3 fraction was higher when the losses were more pronounced in the initial pulses. However, the variation in catalyst activity over the first few pulses (Table 1) and the detection of faint ESR signals in used catalyst, probably due to graphitic structures (*25*), imply that coking also occurs. It is also significant that hydrocracking of the side chains is not an important reaction, especially with indene, which gave substantial losses even at lower temperatures. Condensation of aromatic nuclei on supported metals has been recorded previously (*26*) and cyclopentadiene has been suggested as a possible intermediate in coke formation under reforming conditions (*27*).

The activity of the C_5 ring in this respect may explain the higher losses from indane than from other compounds where the C_5 ring is not already formed. There seems no reason why the postulated π-bonded intermediates for ring closure could not undergo intermolecular reaction as well. This would lead to a build-up of polynuclear aromatics strongly adsorbed through multiple π-bonding. These reactions quickly coke the surface of the fresh catalyst so that the major changes occur in the first few pulses. The most active sites for condensation, coke formation, and hydrocracking are eliminated and although the catalyst becomes less active it is more selective for dehydrocyclization.

Thermal sintering of the catalyst appears to have a similar effect on the more active centers because the initial pulses on sintered catalysts (Table 5) give lower losses. Initial pulses on catalyst which had received prolonged heat treatment at 480°C (Table 6) not only gave lower losses but also increased yields of transformed products.

The reactions in which thiophene was admitted to the catalyst show that the sulfur compound is more strongly chemisorbed than the hydrocarbons and that adsorption is only partly reversible. Approximately the same level of activity was reached using both methods of poisoning (see Figs. 2 and 3) and at this point further addition of thiophene had little or no effect. This suggests that thiophene does not completely poison the catalyst and may only be strongly adsorbed on highly active centers. Previous work has shown that thiophene selectively poisons the hydrogenating activity of platinum for benzene but not for olefins (*28*). We believe that the sites poisoned in this way are those highly active for ring formation, condensation, and coking. This view is supported by the observation that thiophene suppresses hydrocarbon losses and indane formation (Fig. 2) but initially enhances the yields of *o*-ethyltoluene, arising from the rupture of the C_5 ring (Figs. 2 and 3). The latter effect may be due to suppression of side reactions of C_9 intermediates and perhaps to selective retardation of the back reaction of ring closure. While hydrogenolysis may also occur on the same centers as those involved in ring closure it is possible that cleavage of indane to *o*-ethyltoluene can also take place on those sites which are active for hydrogenation of olefins and are not so greatly affected by thiophene adsorption. The apparent increase in hydrogenolysis activity must not be associated with an absolute increase in activity for ring opening as thiophene did not enhance the hydrocracking of ω-methylstyrene to toluene in the initial pulses (Fig. 3). It has been reported previously (*29*) that sulfur poisons tend to increase hydrocracking on reforming catalysts but this has been attributed to increased acidity function.

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