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Retained Products from the Reaction of Benzene and Toluene over H-ZSM5 Zeolite

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Benzene or toluene react on H-ZSM5 zeolite in the absence of added oxygen at 593 K and 673 K to give retained residue which contains some anthracenes/(phenanthrenes) accompanied by biphenyls, diphenylmethanes, fluorenes, alkanes/(olefins), alkylbenzenes, alkylnaphthalenes, and (at 673 K) some black insoluble carbonaceous polymer; it is inferred that the condensation reactions which have been identified as leading to fused-ring tricyclic aromatics form part of the pathway to this carbonaceous polymer. The retained aromatic components mostly carry methyl substituents. It is concluded that anthracenes/(phenanthrenes) are formed from benzene or toluene via biphenyls (the primary condensation product) and diphenylmethanes, the presence of methyl (or other alkyl) substituents being a necessary feature. This reaction may be a general one for the enlargement of fused, polycyclic, aromatic systems. In the presence of oxygen, the retained hydrocarbon products are generally similar to those formed without added oxygen, although aromatic oxygenates are coproduced. Reaction pathways are discussed.

INTRODUCTION

During the conversion of 1-hexene over H-ZSM5 zeolite, organic residue can be retained by the catalyst in addition to products which are returned to the gas phase; the composition of this residue, its mode of formation, and its evolution at higher temperatures to fused-ring aromatics have been studied in detail (*1*).

The purpose of the present work was to examine if, over H-ZSM5 zeolite, condensation reactions could occur from simple monocyclic aromatics such as benzene or toluene leading to retained fused-ring products, since this could provide a pathway to fused-ring aromatics (and ultimately to coke) additional to those outlined previously (*1*).

The formation of fused-ring aromatics by ring condensation reactions has a long history over Friedel–Crafts-type catalysts (*2*, *3*), and may be considered as a specialization of the generalized Scholl reaction (*4*). This type of reaction is known to be assisted by the presence of homosystemic or heterosystemic hydrogen acceptors.[3] The present report deals mainly with homosystemic hydrogen acceptors, but some studies have also been performed in the presence of oxygen, the latter being a common heterosystemic hydrogen acceptor used in the Scholl reaction (*4*).

The present work is mainly concerned with the reactions of benzene and toluene over H-ZSM5 but, as an example of the behavior of a low acidity material, toluene was also examined over silicalite. To help eluci-

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[3] Heterosystemic indicates a hydrogen acceptor which is added to the reaction system specifically for that purpose; homosystemic indicates a hydrogen acceptor which is already present as an intrinsic component of the condensation reaction (e.g., reactant).

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date the mechanism of the reactions of benzene and toluene, the reactions of 3,3′-dimethylbiphenyl, methyldiphenylmethane (a mixture of 4-methyl and 3-methyl isomers), 9-methylfluorene, 9-ethylfluorene, 9,10-dihydroanthracene, and anthracene were also examined over H-ZSM5.

It should be noted that the treatment conditions used in the present work were directed toward a study of the residue-forming reactions per se, rather than to a demonstration that the present results *necessarily* apply to any particular catalytic process.

EXPERIMENTAL

The method of treatment of H-ZSM5 with organic reactant, and the methods of product analysis were essentially similar to those previously described (*1*). Liquid reactant was fed from a motor-driven syringe (0.27 $cm^3 h^{-1}$ liquid) via a heated vaporizer into a carrier gas stream (20 $cm^3 min^{-1}$) which was either high-purity nitrogen (oxygen-free, $\leq$10 ppm impurity), or the same nitrogen gas to which oxygen was added. In the case of 9-methylfluorene (mp 316 K), 9,10-dihydroanthracene (mp 382 K), and anthracene (mp 490 K), the carrier gas stream was passed over a bed of reactant at ca. 473 K to give an estimated reactant pressure of ca. 3.5 kPa, equivalent to a feed rate of ca. 0.6 $g h^{-1}$ with nitrogen carrier gas at 1 atm. and 20 $cm^3 min^{-1}$. Heated transfer lines were used.

A down-flow reactor containing 1.0 g of zeolite supported as a ca. 3-mm-thick bed on a frit was used. Treatment times were in the range 45–120 min. Detailed reaction conditions are specified with the results.

Analysis of retained residue was by GC–MS and GC following an acid-dissolution/solvent extraction method to recover the residue from the zeolite (*1, 7*). Blank experiments (cf *1*) showed that this residue recovery method was without effect on all of the main reactant and product classes, in agreement with previous work on other and related systems (e.g., *1, 7, 40*).

A search for possible nitrogenous compounds in the retained product was made using a GC with a nitrogen-specific detector (thermal ion specific detector). The minimum detectable level of nitrogen was estimated as about 6×10^{-9} g N, assuming a minimum identifiable signal on the recorder trace to be about ×3 noise.

Zeolite. H-ZSM5 was the same as that previously used (*1*), and was prepared and characterized by standard methods (XRD, scanning and transmission electron microscopy, pore volume measurement, and elemental analysis). XRD data were the same as given in the literature (*8*), measured pore volume was 0.15 $cm^3 g^{-1}$, SiO_2/Al_2O_3 ratio 46/1, and the zeolite consisted of crystals of average size ca. 2 μm associated into aggregates. Silicalite was prepared as previously described (*9*).

Before reaction, the catalyst was first pretreated at 773 K *in situ* in an oxygen stream (20 $cm^3 min^{-1}$, high purity) for 2 h, then flushed in the working carrier gas stream at 773 K for 2 h, and cooled to the intended reaction temperature.

Reactants. Benzene and toluene were high purity analytical grade, (BDH); GC analysis gave toluene (0.12 ± 0.02 wt%) as the only significant impurity in the benzene, and with benzene (0.05 ± 0.02 wt%) and xylenes (0.04 ± 0.02 wt%) as the only significant impurities in the toluene. 3,3′-Dimethylbiphenyl, 9,10-dihydroanthracene, and anthracene were reagent grade (Aldrich). Literature methods were used for the preparation and purification of 9-methylfluorene (*10*), 9-ethylfluorene (*10*), and methyldiphenylmethane (*11*). Although the literature method (*11*) was reported to give 4-methyldiphenylmethane, GC-MS and ^1H NMR analysis clearly showed the purified product to consist of two isomers assigned as 4-methyl and 3-methyl in comparable proportions: the isomer mixture was used without separation.

The total organic content of the treated catalyst was determined by oxidative burnoff (in air) using a microbalance with a linear

TABLE 1

Products from H-ZSM5 Treated with Benzene and with Toluene: Oxygen-Free Conditions[a]

Reactant and temp. (K)	Residue products[c,d]							Insoluble carbonaceous residue	Gaseous products
	Alkanes/ (olefins)	Alkyl-benzenes[f]	Alkyl-naphthalenes	Alkyl-fluorenes	Alkyl-biphenyls	Alkyldiphenyl-methanes	Alkyl-anthracenes/ (phenan-threnes)		
Benzene 593	Medium (1–20)[b,e,l]	Medium (7–13)	Trace (11)	Medium (13–15)[g,h,i]	Medium (13–15)[g]	Medium (14–15)[g]	Small (14–15)	No	—
Benzene 673	Medium (1–18)[e,l]	Medium (7–13)[j]	Medium (14–16)[g]	—	—	Small (13–15)	Small (14–15)	Yes	Benzene (unconverted reactant) plus trace toluene (<0.1%).
Toluene 593	Medium (1–18)[e,l]	Small (6–12)[k]	— —	Medium (13–15)[g,h,i]	Medium (13)	Small (14)	V. small (14)	No	—
Toluene 673	Medium (1–18)[e,l]	Medium (6–15)[k]	Medium (13–15)[g]	—	—	Medium (14–15)[g]	Small (14–15)	Yes	Toluene (unconverted reactant) plus benzene and xylenes (total 4%): $B:X = 1$ molar ratio.

Note. [a] Feed rates—hydrocarbons 0.27 $cm^3\ h^{-1}$ (liq.), N_2 (Oxygen-free) 20 $cm^3\ min^{-1}$; [b] total carbon number range in brackets; [c] from acid dissolution/solvent extraction; [d] trace < 1%, v. small 1–5%, small 6–10%, medium 11–30%, large > 30%; [e] some lower homologues may have been present but escaped estimation; [f] not including unconverted reactant; [g] mainly methyl substituents; [h] v. small proportion 9-(C_2H_5)-fluorene; [i] (CH_3)-fluorene substituted in benzenoid- and q-positions; [j] toluene dominant; [k] benzene and xylenes dominant; [l] mainly 8–18.

temperature ramp in the manner previously described (*1*).

RESULTS

Reactions without Added Oxygen

Experiments at 513 K showed that the extent of benzene and toluene conversion on H-ZSM5 was so small that the level of residue formation and product composition could not be reliably detected or measured. For reactions at 593 K and 673 K, the compositions of evolved and retained residue products are contained in Table 1. The relatively low level of residue (cf Table 2) resulted in considerable degradation of analytical accuracy, and accordingly Table 1 presents the data on a semiquantitative basis.

In the case of benzene reactant, the evolved gaseous products consisted almost entirely of unreacted benzene, while with toluene reactant the gaseous products contained benzene and xylenes from the expected disproportionation reaction, in addition to unreacted toluene.

The retained residue products from both benzene and toluene contained a range of aromatic condensation components and alkane/(olefin) hydrogen-acceptor products. In addition, reactions at 673 K resulted in the formation of some particulate black residue insoluble in the acid-dissolution/solvent extraction process: this was presumably carbonaceous polymer similar to that recently reported from the reaction of *n*-heptane at 723 K on several zeolites (*12, 13*). Because of the small scale of the present reactions, we have not been able to quantitatively estimate this insoluble carbonaceous polymer. Nevertheless, since this material probably had a low H/C ratio (cf. analogous material recovered from other zeolite/hydrocarbon systems—H/C ≤ 0.5 from *n*-heptane at 723 K on H-ZSM5, H-USY, H-offretite (*12, 13*)), its formation probably contributed to alkane/(olefin) hydrogen-acceptor product.

TABLE 2

Organic Residue Content of H-ZSM5 after Treatment with Benzene and with Toluene

Treatment conditions	Organic residue/ wt%
Oxygen-free carrier gas	
Benzene, 90 min, 593 K	0.4
Benzene, 90 min, 673 K	1.2
Toluene, 90 min, 593 K	0.4
Toluene, 120 min, 673 K	1.2
O_2/N_2 = 1/99 (vol.) carrier gas	
Benzene, 90 min, 673 K	1.2
Toluene, 120 min, 593 K	1.9
Toluene, 120 min, 673 K	3.2

Values for the total amount of retained organic residue for H-ZSM5 treated with benzene and toluene are given in Table 2 for the temperatures 593 K and 673 K. At the benzene and toluene feed rates, these levels of retained residue correspond to the conversion of 1–3% of reactant to residue (after allowing for unconverted reactant recovered with the residue).

Table 3 gives the composition of retained products from the reaction on H-ZSM5 of 3,3′-dimethylbiphenyl, 3/4-methyldiphenylmethane, 9-methylfluorene, 9-ethylfluorene, 9,10-dihydroanthracene, and anthracene. These reactants were chosen as models for classes of reaction products from benzene and toluene (Table 1), with particular interest in the extent to which they may be intermediates in the route to fused-ring aromatics.

Reactions with Added Oxygen

Reactions were carried out using a carrier gas containing 1% O_2 (vol) in nitrogen at 593 K and 673 K. Table 2 contains data for the total amount of retained product formed from benzene and toluene over H-ZSM5, and the values correspond to the conversion of ca. 3–8% of the reactant.

The presence of oxygen in the nitrogen carrier gas resulted in the formation of oxygenates in the retained product in addition to hydrocarbons; the composition is given in Table 4.

TABLE 3

Products from H-ZSM5 Treated with Various Aromatics: No Added Oxygen[a]

Reactant and temp. (K)		Residue products[c,t,u]							Insoluble carbonaceous residue	Unconverted reactant in retained residue	Gaseous products
		Alkanes/ (olefins)	Alkyl-biphenyls	Alkyl-diphenyl methanes	Alkyl-fluorenes	Alkyl-anthracenes/ (phenanthrenes)	Higher aromatics	Miscellaneous			
3,3′-Dimethylbiphenyl	593	Small (16–20)[b]	Medium (13–16)[d]	Medium (13–14)	Large (14–17)[e]	Small (14–17)[f]	—	—	No	~30%	—
	673	Small (≥16)	Medium (15)	Medium (13–14)[g]	Medium (13–16)[h]	Medium (14–18)[i]	—	—	Yes	—	—
3/4-Methyldiphenylmethane	593	—	—	Trace (17)[j]	Large (13–16)[k]	Small (14–17)	—	Small (20–22)[l]	Trace	~10%	Benzene, toluene, xylenes
9,10-Dihydroanthracene	593	—	—	Medium (14)	—	Large (14)[m]	—	Large (14)[n]	Trace	~20%	—
Anthracene	593	—	—	—	—	—	—	—	Trace	~100%	—
9-Methylfluorene	593, 673	Trace	—	—	Trace[o]	—	—	—	No	~100%	V. small amounts 9-methylenefluorene
9-Ethylfluorene	593	—	Small (13–15)[j]	Small (15)	Large (13–18)[p]	Large (14–19)[q]	Small (17)[r]	V. small (15)[s]	No	~60%	V. small amounts methylfluorene, dimethylbiphenyl, alkanes, olefins

Note. [a]Feed rates—3,3′-dimethylbiphenyl, 3/4-methyldiphenylmethane, 9-ethylfluorene 0.27 cm^{3}h^{-1} (liq.); 9,10-dihydroanthracene, anthracene, 9-methylfluorene ca. 0.6 g h^{-1}; N_2 (oxygen-free) 20 cm^3 min^{-1}; [b]total carbon number range in brackets; [c]not including reactant; [d]methyl substituents, mainly $(CH_3)_3$- and $(CH_3)_2$-, (CH_3)-fluorene benzenoid substituted; [f]mainly (CH_3)-, $(CH_3)_2$-, $(CH_3)_3$; [g]mainly (CH_3)-; [h]methyl substituents, mainly (CH_3)-, $(CH_3)_2$-; (CH_3)-fluorene ca. 50% 9-(CH_3)-; [i]mainly (CH_3)-, $(CH_3)_2$-; [j]methyl substituents; [k]mainly (CH_3)-, $(CH_3)_2$-; 9-(C_2H_5)-fluorene trace only; [l]three components with parent (*m*/*e*) at 258, 272, 286—mass spectra suggest -$(CH_3)_n$ (n = 0, 1, 2); [m]ca. 20% phenanthrene and 80% anthracene; [n]tetrahydroanthracene/phenanthrene; [o]fluorene; [p]mainly methyl substituents; [q](CH_3)- ca. 65% of total, mainly phenanthrenes; [r](CH_3)-pyrene, dihydropyrene, (CH_3)-dihydropyrene; [s]9-ethylidenefluorene; [t]trace < 1%, v. small 1–5%, small 6–10%, medium 11–30%, large >30%; [u]from acid dissolution/solvent extraction.

TABLE 4

Products from H-ZSM5 Treated with Benzene and with Toluene: Oxygen-Containing Conditions (O_2/N_2 = 1/99, vol)[a]

Reactant and temp. (K)	Residue products[c,d]									Insoluble carbonaceous residue
	Alkanes/ (olefins)	Alkyl-benzenes[f]	Alkyl-naphthalenes	Alkyl-fluorenes	Alkyl-biphenyls	Alkyl-diphenyl-methanes	Alkyl-anthracenes/ (phenanthrenes)	Other aromatics	Oxygenates[j]	
Benzene 673	Small (8–16)[b,e]	V. small	—	Small (13–14)[g]	—	V. small (13)	Medium (14)	V. small (16, 19)[i]	Large	Yes
Toluene 593	V. small (8–16)	V. small	V. small (15–16)[g]	Medium (13–15)[g]	—	V. small (15)[g]	Medium (14–15)[g]	—	Large	Yes
Toluene 673	Trace	V. small	V. small (11–14)[g]	Medium (13–14)[g]	—	Small (13–16)[g]	Small (14–16)[g]	—	Large	Yes

Note. [a]Feed rates—hydrocarbon 0.27 $cm^3\ h^{-1}$ (liq.), (N_2 + O_2) 20 $cm^3\ min^{-1}$; [b]total carbon number range in brackets; [c]from acid dissolution/solvent extraction; [d]trace <1%, v. small 1–5%, small 6–10%, medium 11–30%, large >30%; [e]some lower homologues may have been present but escaped detection; [f]not including unconverted reactant; [g]mainly methyl substituents; [h](CH_3)-fluorene substituted in benzenoid- and 9-positions; [i]pyrene and benzopyrene; [j]main oxygenate components in decreasing order of importance—monohydroxyaromatics (alkylphenols, alkylnaphthols, hydroxyalkylbiphenyls), alkylfluorenones, alkylanthrones, alkyldibenzofurans, an unidentified oxygenate (possibly an aromatic aldehyde), other minor oxygenates (alkyldiphenylethers, alkylbenzaldehydes, benzofuran).

The reaction of toluene was also examined over silicalite (673 K, 120 min). The amount of retained residue was barely above the detectable minimum, and only some unreacted toluene could be identified. The result indicates that, even in the presence of oxygen in the carrier gas, catalyst acidity is necessary for the formation of aromatic condensation products at this reaction temperature.

No nitrogen-containing components could be detected in any of the retained reaction products out to the limit of the GC temperature program (ca. C_{20}). Using benzo[*c*]cinnoline ($C_{12}H_8N_2$) as an example, the minimum detectable level of nitrogen (ca. 6×10^{-9} g) with the analytical technique used, would correspond to a minimum detectable level of benzo[*c*]cinnoline in the retained product of ca. 0.4 wt%.[4]

DISCUSSION

Reactions without Added Oxygen

General features. Table 1 shows that both benzene and toluene yielded biphenyls, diphenylmethanes, fluorenes, and anthracenes/(phenanthrenes) as condensation products, accompanied by alkanes/(olefins),[5] alkylbenzenes, and, at higher temperatures, naphthalenes. Alkanes were the ultimate homosystemic hydrogen acceptor products, being (presumably) formed from acid-catalyzed reactions involving ring opening in a partly hydrogenated benzene ring, followed by facile olefin oligomerization/cracking and hydrogen transfer. It should be noted that under the present conditions, the fraction of benzene or toluene reactant converted to retained residue is relatively small (1–3%) and, of the retained residue, the anthracenes/(phenanthrenes) comprise a small component (<ca. 10%). Comparison of the present results with those obtained using 1-hexene reactant (*1*) shows that the residue-forming propensity of simple aromatics such as benzene or toluene with H-ZSM5 is much less than that of olefins, in agreement with the proposal previously made by Venuto *et al.* (*40*).

In the temperature regime of the present work, the presence of alkane/(olefin) components makes inevitable the occurrence of facile acid-catalyzed alkylation reactions, leading to the formation of alkylbenzenes (Table 1), with side-chain cracking also contributing to the wide range of alkyl substituents. The naphthalenes arise, we suggest, from cyclization in suitable alkylbenzenes (a known acid-catalyzed reaction (*14*) which we have confirmed using the reaction of *n*-butylbenzene over H-ZSM5 at 593 K in which naphthalene, methylnaphthalene, and dimethylnaphthalene comprised about one-third of the non-alkylbenzene retained residue).[6]

An important feature of the present reaction is that the biphenyls, diphenylmethanes, fluorenes, and anthracenes/(phenanthenes) mostly have one or more methyl substituents, while toluene was the dominant alkylbenzene constituent from the reaction of benzene. When using benzene reactant, we attribute this formation of methyl substituents to the occurrence of alkylation/side-chain cracking reactions, but with toluene reactant methyl substituents would clearly also have been carried through from the initial reactant. The generation of methyl substituents by alkylation/side-chain cracking in this way can only occur at an appreciable extent of reaction (since alkane/(olefin)

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[4] Using data given by Benson (*32*), we estimate $\Delta G^\circ_{f,600}$ for benzo[*c*]cinnoline to be 613 ± 20 kJ mol^{-1}; thus, for the hypothetical reaction $2C_6H_6 + N_2 + O_2 \rightarrow C_{12}H_8N_2 + 2H_2O$ we estimate ΔG°_{600} to be -179 ± 20 kJ mol^{-1}. The formation of benzo[*c*]cinnoline has been claimed (*6*) during the partial regeneration by air oxidation of a coked chabazite catalyst.

[5] Alkanes/(olefins) indicates that this product was mainly alkane but with evidence for a small proportion of olefins which could not be separately estimated.

[6] Under high-temperature, acid-catalyzed conditions, the occurrence of relatively facile cracking, oligomerization, and alkylation reactions will result in the effective reactant being alkylbenzene with a range of chain lengths.

alkylation reactants are not initially present), and when the reaction products are largely retained by the catalyst (otherwise in a flow system at low overall conversion the observed products would be initial products). An analogous type of reaction to yield alkylated (particularly methylated) products has previously been reported (*15*) for the conversion of benzene over a HF/TaF_5 catalyst at 473 K, for which a similar pathway was adduced.

The data (Table 1) are semiquantitative preventing an accurate conservation in H/C ratio,[7] although at 593 K an approximate conservation in H/C is possible within the indicated composition ranges.

The present results differ from those previously reported for the Scholl reaction (*4*) with Friedel–Crafts-type catalysts in two main ways, both of which result from the Scholl reaction being generally carried out under considerably milder conditions. The Scholl reaction tends to be limited to the formation of the initial coupling product (although complete product analyses were never reported, presumably due to analytical inadequacy at the time), and product alkylation/side-chain cracking reactions were minimal. Thus, the reaction of benzene with an aluminium chloride catalyst under various reaction conditions in the range ca. 300–473 K (*4*) gave biphenyl as the main reported product, together with homosystemic hydrogen acceptor products such as phenylcyclohexane.

Examples of the Scholl reaction involving direct condensation between aromatic nuclei to yield polycyclic, fused-ring aromatics are known, for instance: chrysene and benzene to give 1,2 : 4,5-dibenzopyrene (*16*), or self-condensation reactions such as naphthalene to perylene (*17*), phenanthrene to 2,3 : 10,11-dibenzoperylene (*18*), and chrysene to dinaphthoperylene (*19*). An analogous reaction from benzene alone would require the self-condensation of three benzene nuclei to yield triphenylene. In fact, the formation of triphenylene in this way under Scholl reaction conditions using Friedel–Crafts-type catalysts does not appear to have been reported, although the formation of triphenylene from *o*-terphenyl is known (*20*), and the latter can probably be prepared by the Scholl reaction from benzene under special conditions (*21*). Nevertheless, the direct condensation of benzene to triphenylene has been suggested as an archetypal condensation reaction leading to fused-ring, polycyclic aromatics (*22*). A careful search in the present work never revealed the presence of any triphenylene[8] or its methyl derivatives, and we conclude that, at least under the present conditions, this reaction is not significant.

Table 3 shows that diphenylmethanes and anthracenes/(phenanthrenes) were formed from 3,3′-dimethylbiphenyl over H-ZSM5 (593 K, 673 K), while anthracenes/(phenanthrenes) were formed from 3/4-methyldiphenylmethane but no biphenyls were formed (593 K). Both of these reactants also yielded fluorenes, although these were probably by-products of the reaction to anthracenes/(phenanthrenes) (vide infra). We thus suggest that the immediate precursor to the anthracene/(phenanthrene) system was 2-methyldiphenylmethane (**B**, Figure 1) which could be formed either from a 2,*x*′-dimethylbiphenyl (**A**) or by direct condensation from toluene (cf. Fig. 1): the latter route recognizes that this condensation is already accepted as being involved in toluene disproportionation (*23–25*). Our data do not provide a definitive answer as to the relative

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[7] Even at 593 K when no black, insoluble, residue was formed, there is the possibility of soluble but relatively involatile components (e.g., higher polycyclic aromatics with low H/C) which might have escaped analysis.

[8] The reaction $3C_6H_6 \rightarrow C_{18}H_{12} + 3H_2$ has $\Delta G^\circ_{673} = +14$ kJ mol^{-1} for the gas phase (and is less favorable at this temperature if benzene is a homosystemic hydrogen acceptor and *n*-C_6H_{14} the acceptor product); however, the observation of triphenylene would probably not be thermodyamically prevented if the triphenylene was sorbed on the catalyst (cf. text, thermodynamic considerations).

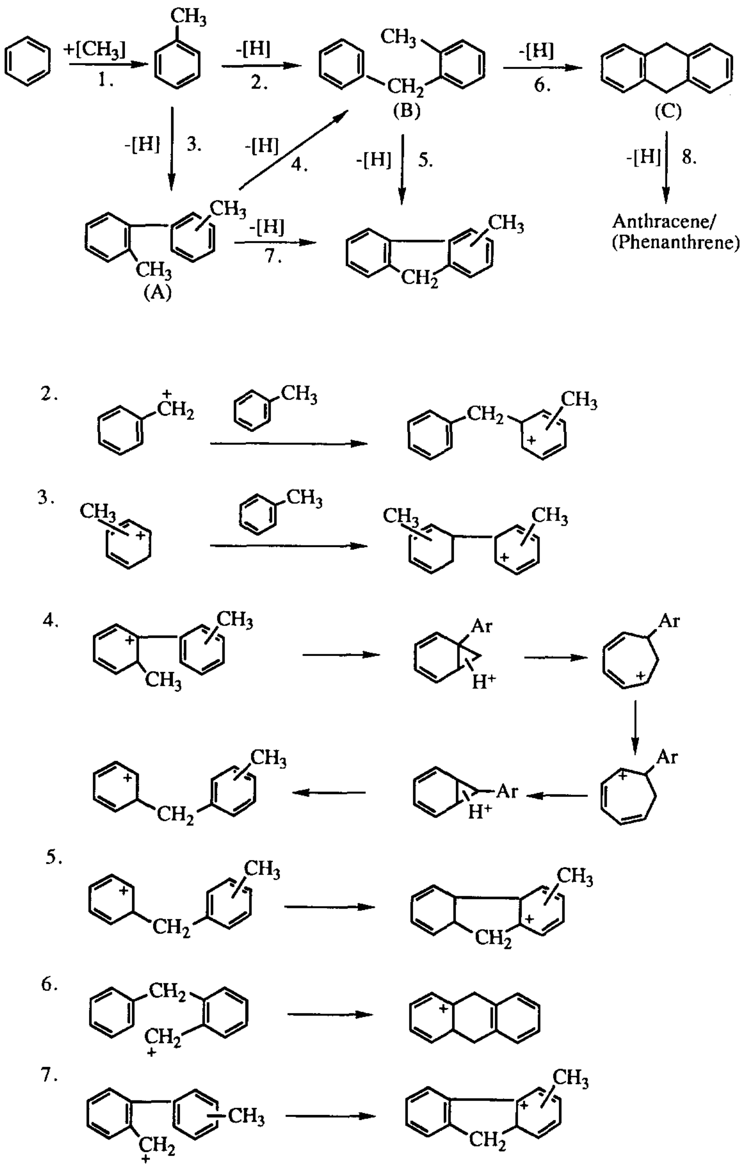

FIG. 1. Schematic route for the conversion of benzene or toluene to anthracene/(phenanthrene). $+[CH_3]$ indicates the introduction of $-CH_3$ via alkylation/side-chain cracking, and $-[H]$ the removal of one or more H, both processes being Brønsted acid mediated. Variants to the main reaction are possible depending on which point in the sequence benzenoid methylation occurs. The formation of a fluorene methylated at the 9-position (an observed product) may occur by an alkylation/cracking reaction (not shown).

importance of these two routes, but both probably contributed. In the reaction scheme summarized in Fig. 1, it should be noted that under acid-catalyzed conditions, aromatic methyl substituents will be mobile around benzenoid rings, thus providing ample *ortho* occupation as required in the biphenyl (**A**) and in the diphenylmethane (**B**).

In connection with the mechanism proposed in Fig. 1 for the formation of an anthracene skeleton (**C**) from 2-methyldiphenylmethane (**B**), it has previously been reported (*26, 27*) that anthracenes are formed from diarylmethanes under Scholl reaction conditions although the mechanism was not clear (*4*).

Phenanthrene is thermodynamically favored over anthracene (ΔG°_{600} is -26 kJ mol^{-1} for anthracene → phenanthrene). Nevertheless, the conversion of anthracene to phenanthrene does not occur over H-ZSM5 (593 K, cf. Table 3), nor does it occur using aluminum chloride (*28*) or antimony trichloride catalysts (*29*) ($AlCl_3$, 293–343 K, up to 20 h; $SbCl_3$, 343–423 K, up to 7 h; both anaerobic conditions). However, the conversion of an anthracene skeleton to that of phenanthrene is well known in partly hydrogenated species (e.g., octahydroanthracene to octahydrophenanthrene over BF_3/HF at 273–323 K (*30*)), and Table 3 shows that some phenanthrene can be formed from 9,10-dihydroanthracene over H-ZSM5 at 593 K (skeletal rearrangement with dehydrogation). This result is consistent with the presence of some phenanthrenes in addition to anthracenes in our tricyclic aromatic products.

Table 3 also shows that 9-methylfluorene, a significant retained product component from benzene and toluene of 593 K, had little reactivity over H-ZSM5 at 593–673 K, with no biphenyls, diphenylmethanes, or anthracenes/(phenanthrenes) being formed. Thus, under these conditions 9-methylfluorene cannot be an intermediate in the conversion of 3,3′-dimethylbiphenyl to diphenylmethanes, nor can it be a precursor to the formation of the anthracene/(phenanthrene) skeleton. On the other hand, phenanthrenes comprised a major product component from the reaction of 9-ethylfluorene on H-ZSM5 at 593 K (Table 3). However, 9-ethylfluorene was not more than a trace product from the reactions of benzene and toluene, and we conclude that it did not therefore provide a significant reaction pathway. The enhanced reactivity of 9-ethylfluorene for C_5 ring enlargement compared with 9-methylfluorene is expected from the involvement of a secondary carbenium ion in the reaction of the former.

The individual steps in the reaction scheme of Fig. 1 can be formulated in terms of standard carbocation chemistry, as indicated. A radical-ion mechanism has been suggested for the Scholl reaction (*33*), but on balance seems less likely (*4*).

In addition to the mechanism suggested, step 4 can also be readily formulated as involving primary carbenium ions: we suggest the route shown for reasons of probable energetic economy. Steps 2, 6, and 7 necessarily involve benzylic type carbenium ions which are energetically accessible intermediates (*36, 37*).

Locus of reactions. Benzene and toluene have molecular dimensions which allow ready transport in the channels of H-ZSM5. Anthracene, 9,10-dihydroanthracene, fluorene (all ca. 1.01 × 0.58 nm),[9] methylanthracenes and methylfluorenes with nonapical substituents, all would be expected to have at best only marginal mobility. 2,*x*′-Dimethylbiphenyl, 2-methyldiphenylmethane (both ca. 1.03 × 0.60 nm), 3/4-methyldiphenylmethane (ca. 1.17 × 0.60 nm), phenanthrene (ca. 1.01 × 0.64 nm), methylphenanthrenes, methylanthracenes, and methylfluorenes with apical substituents, all have dimensions which preclude channel transport. 3,3′-Dimethylbiphenyl (ca. 1.01 × 0.66 is too large to allow transport, but acid-catalyzed isomerization to (inter alia) the 4,4′-isomer would be relatively rapid. In addition, examination of scale models suggests that, of the molecules listed above, all could be accommodated at channel inersections in H-ZSM5, with the probable exceptions of phenanthrene, methylphenanthrenes, meth-

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[9] Critical molecular dimensions obtained by scaling dimensions of Catalin models to values given by Fraenkel *et al.* (*39*). In the case of methyldiphenylmethanes and 2,*x*′-dimethylbiphenyl, the assumed molecular configurations were those giving the minimum dimensions.

ylanthracenes, and methylfluorenes with apical substituents, and 3,3′-dimethylbiphenyl.

As a consequence, we conclude that the channel intersections are the main probable loci for the condensation reactions occurring from benzene and toluene, the polycyclic products being trapped within the zeolite, but some reaction may well have also occurred on the external surface. The reaction of 3,3′-dimethylbiphenyl probably occurred both internally and externally, the internal reaction being preceded by external isomerization to the 4,4′-isomer which would be mobile in the channels. Reactions of 3/4-methyldiphenylmethane and 9,10-dihydroanthracene would be expected to have occurred mainly at the external surface.

So far as a comparison is possible, our results recorded above agree with those given in the brief previous report (*5*) of the reaction at 743–763 K of benzene over a high-silica zeolite-styled ZHM. This work used a zeolite/benzene ratio ca. 0.1–0.5 in what was apparently either a closed static system or a recirculating system. Only products returned to the gas phase were examined, and those were reported as alkylbenzenes and naphthalene. No examination was apparently made for products retained with the catalyst.

Thermodynamic considerations. The basic reactions in Fig. 1 may be modeled in a number of ways which differ in detail. We have evaluated ΔG° (T = 300–800 K) for the various component reactions between toluene and anthracene, assuming the component reactions specified in Fig. 2, and that all species are gaseous. All thermodynamic data were taken from the standard literature (*31*) except for 2-methyldiphenylmethane for which $\Delta H^\circ_{f,298}$, S°_{298}, and $C_{p,298}$ were calculated using Benson's method (*32*), with values of $\Delta G^\circ_{f,T}$ being obtained using a temperature-dependent C_p, the latter being estimated using the calculated $C_{p,298}$ and the literature values of $C_{p,T}$ for 3,3′-dimethylbiphenyl.

Figure 2 shows that although the interme-

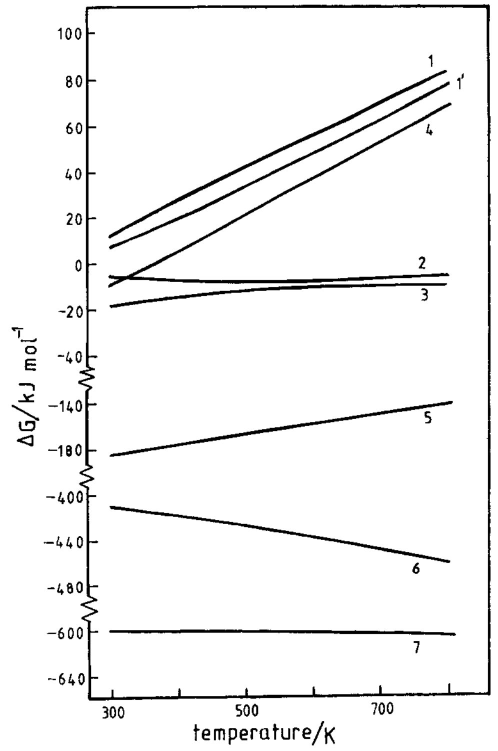
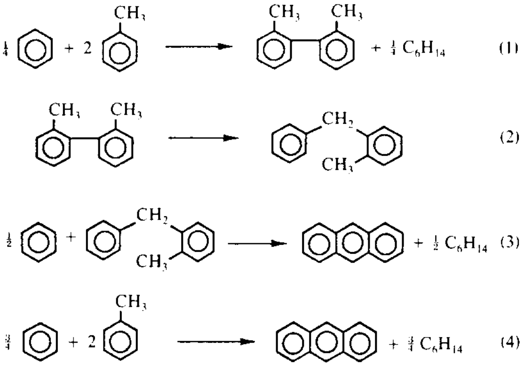
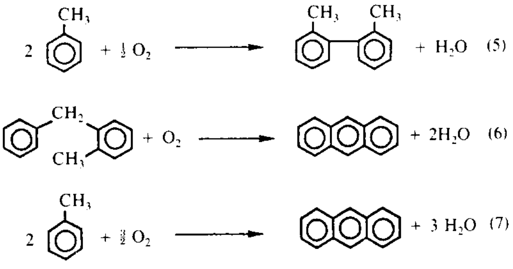


FIG. 2. Standard free-energy changes for reactions:



where (4) is the overall reaction (sum of reactions (1)–(3)) and (1′) is the sum of reactions (1) and (2).



where (7) is the overall reaction (sum of reactions (5), (2), and (6)).

diate reactions (2) and (3) have negative ΔG° values at all temperatures, the initial reaction (1) for the formation of 2,2′-dimethylbiphenyl is unfavorable at all temperatures, as is the formation of 2-methyldiphenylmethane (curve 1′ for the sum of reactions (1) and (2)): as a consequence the overall reaction (4) only has negative ΔG° values below about 370 K, and for instance ΔG° for reaction (4) is $+36$ and $+48$ kJ mol^{-1} at 593 and 673 K, respectively.

The component reactions specified in Fig. 2 assume that benzene is the homosystemic hydrogen acceptor, with n-C_6H_{14} being the hydrogen acceptor product. If other alkanes (C_n, $n > 4$) are assumed as the hydrogen acceptor products, the overall thermodynamics are not significantly improved, and they are worse if alkenes (e.g., 1-hexene) are assumed. The assumption of cyclohexane gives considerably improved thermodynamics (ΔG° values for the overall reaction -120 and -140 kJ mol^{-1} at 593 and 673 K respectively), but cyclohexane was not an observed product.

The data suggest that, under the present reaction conditions (593 K, 673 K), the extent of formation of the intermediate biphenyls and diphenylmethanes is probably thermodynamically limited; further conversion to anthracenes/(phenanthrenes) would appear to be kinetically controlled. Indeed, with positive values for ΔG° for reactions (1), (1′), and (4) (Fig. 2), we suggest that the reactions are observable at the present levels because the reaction products are accumulated with the H-ZSM5 catalyst. For instance, if product trapping was equivalent to a reduction of the product vapor pressure by a factor of 10^3 compared with the gas phase equilibrium values, this would be equivalent to a reduction in ΔG° for the overall reaction, via a term $RT \ln (p_1/p_2)$, by ca. 34 kJ mol^{-1} at 593 K.

Reactions with Added Oxygen

The dominant effect of using the oxygen-containing carrier gas was the generation of substantial amounts of aromatic oxygenates in the retained products. The formation of hydrocarbon products was relatively insensitive to the addition of oxygen at a 1% (vol) level (an oxygen level of 1% vol represents an increase by a factor of $\not< 2 \times 10^3$ compared with the maximum oxygen impurity level in the high purity nitrogen). Thus, the total amount of hydrocarbon retained product and the classes of hydrocarbon components were approximately similar with or without the added oxygen. The main effect of the added oxygen on the retained hydrocarbon product distribution was a modest increase (ca. ×2) in the level of anthracenes/(phenanthrenes), and a decrease in the levels of alkanes/(olefins) and alkylbenzenes: most aromatic products were methyl substituted in the two circumstances. Thus, although aromatic condensation reactions are much more favorable thermodynamically when oxygen functions as a heterosystemic hydrogen acceptor (Fig. 2), we conclude from the results summarized above that in the presence of 1% (vol) oxygen a substantial proportion of the reaction leading to hydrocarbon products did not involve oxygen but retained the use of homosystemic hydrogen acceptor.[10]

The chemistry of the formation of the observed oxygenates, including the possible involvement of free-radical processes (*34*, *35*), is discussed in a further report (*38*).

Growth of Larger Fused-Ring Aromatic Systems

Growth of fused-ring aromatic systems from smaller aromatic hydrocarbon precursors can occur in a number of different ways. For acid-catalyzed conditions, we note the possibility of growth by (i) direct condensation of unsubstituted aromatics (e.g., benzene and chrysene to give 1,2 : 4,5-

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[10] The formation of fluorenone proved to be a particularly sensitive indicator for the presence of low levels of (adventitious) oxygen impurity in the nitrogen carrier. In experiments without added oxygen, results were discarded if fluorenone could be detected in the retained product.

dibenzopyrene and similar condensations alluded to previously), and (ii) condensations involving alkyl substituents on the reacting aromatics in the manner outlined in Fig. 1. This scheme can be generalized for growth at a benzenoid ring which is part of a larger fused-ring system provided no steric impediments are present.

Although the reaction scheme in Fig. 1 has been written in terms of methyl substituents, similar processes would be possible (indeed more facile) if the substituents were C_n ($n > 1$), but would then result in products carrying C_m ($m = n - 1$) alkyl substituents. It should also be noted that if an alkyl side chain is of sufficient length, the formation of an additional fused benzene ring is possible by side-chain cyclization (cf. previous comments concerning the reactions of *n*-butylbenzene over H-ZSM5).

For benzenoid, fused-ring aromatics (C_n, $6 \leq n \leq 22$), $\Delta G_f^\circ/n$ is approximately constant (range 27.5–31.5 kJ mol^{-1} per C at 600 K). Thus, for a given size of growth increment, ΔG° for the process will be approximately independent of the size of the growing species. However, since the product becomes increasingly involatile as the molecular size increases, the retained product becomes increasingly favorable thermodynamically when judged with reference to a (hypothetical) gas phase situation.

CONCLUSIONS

Over H-ZSM5 at 593–673 K in high-purity nitrogen carrier (no added oxygen), both benzene and toluene reactants yielded retained residues of generally similar composition containing, apart from some unconverted reactant, the condensation products biphenyls, diphenylmethanes, fluorenes, and anthracenes/(phenanthrenes), accompanied by alkanes/(olefins), alkylbenzenes, and alkylnaphthalenes. The alkanes/(olefins) were hydrogen acceptor products which also functioned as alkylation agents under reaction conditions. The aromatics produced from both benzene and toluene mostly carried methyl substituents: in the case of benzene reactant this is attributed to the occurrence of alkylation/side-chain cracking reactions, while with toluene reactant this process would be accompanied by the provision of methyl groups originating in the reactant. The occurrence of substantial alkylation/side-chain cracking is a consequence of product retention with the catalyst so that true initial products were not observed. Only a relatively small fraction (1–3%) of total benzene or toluene feed was converted into retained residue. Below 593 K no reaction products or retained residue, other than unconverted reactant, could be detected.

The addition of a low level of oxygen (1% vol) to the nitrogen carrier resulted in the formation of retained hydrocarbons from both benzene and toluene which were generally of similar character to those formed in the absence of oxygen, but oxygen also resulted in the formation of aromatic oxygenates at a level of total retained residue about 3 times greater. Evidence suggests that in the presence of oxygen at this level, a substantial proportion of the reaction leading to hydrocarbon products retained the use of homosystemic hydrogen acceptor.

Reactions with benzene or toluene at 673 K (oxygen-free) and at 593 and 673 K (1% oxygen) also yielded some particulate black insoluble residue which was probably carbonaceous polymer; we infer that the condensation reactions which have been identified as leading to fused-ring tricyclic aromatics form part of the pathway to this material.

From the nature of the reaction products and the behavior of the model compounds 3,3′-dimethylbiphenyl and 3/4-methyldiphenylmethane, it is concluded that anthracenes/(phenanthrenes) are formed from benzene and toluene via biphenyls (the primary class of condensation product) and diphenylmethanes, with the presence of methyl substituents being a necessary feature. It is suggested that this basic method for the enlargement of an aromatic fused-ring system could be a general one.

The residue products also contained methylfluorenes which appear to be formed via biphenyls but which do not provide a route to anthracenes/(phenanthrenes).

Reaction thermodynamics suggest that under the present conditions, the overall conversion of benzene and toluene is thermodynamically limited, but can be driven by reduced effective volatility of the fused-ring product. In this sense, the reaction becomes thermodynamically more favorable the higher the molecular weight of the product.

Catalyst acidity is essential for the condensation reactions from benzene and toluene, since the use of nonacidic silicalite in place of H-ZSM5 resulted in no reaction, even in the presence of oxygen.

A careful search failed to reveal the incorporation of nitrogen into any reaction product.

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