Low Temperature Hydrogenation of Polycyclic Aromatic Hydrocarbons (PAH's) by Tetralin in a Molten Salt Catalyst*

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Molten $SbCl_3$ has been shown to be an effective catalyst for the hydrocracking of coal with a high selectivity for the production of distillate hydrocarbons (1), analogous to the more extensively studied molten salt hydrocracking catalysts based on $ZnCl_2$ (2,3). Our research is aimed at a basic study of molten salt catalysis with recent studies examining the chemical behavior of PAH's (model compounds for some of the structural units of coal) in molten salts in which $SbCl_3$ is the primary constituent (4-7). We have observed reactions for PAH's in $SbCl_3$ based melts in which the anhydrous $SbCl_3$ solvent is involved catalytically (4) and stoichiometrically (5,6). Both types of chemistry have been explained by redox driven reactions in the melt in which Sb^{3+} is an oxidant.

Tetralin is often used as a hydrogen donor solvent for thermally generated neutral radicals in coal liquefaction and model compound studies. In the present work, we investigate the possibility that tetralin may act as a hydrogen donor to some PAH's under extremely mild (80°C, no H_2) molten salt catalytic conditions in which PAH radical cations are believed to be present as reactive intermediates.

We have studied the reaction behavior of phenanthrene, pyrene, anthracene, and naphthacene (tetracene) with tetralin at 80°C in neat aprotic $SbCl_3$ by in situ ^1H NMR, and by determining the reaction stoichiometry via product analysis following quench and separation procedures. All reagents were carefully purified (4,5), and material transfers were carried out in a controlled argon atmosphere dry box. ^1H NMR experiments (at 200 MH_z) were performed under argon in sealed 5mm OD tubes while larger scale reactions were performed under argon in Schlenk glassware. Following a 30 min reaction period, the reaction mixture was hydrolyzed with 6 M HCl and the organic products were extracted into CH_2Cl_2. $SbCl_3$ is a catalyst in these reactions, and no antimony metal was ever observed. The organic products from the reaction of anthracene with tetralin in $SbCl_3$ were analyzed by GC-MS using a 30 m x 0.25 mm ID glass capillary column with an OV-101 liquid phase. Quantitative results were obtained by GC using a 10' x 1/8" column packed with 3% Dexsil 300 and flame ionization detection. Hexamethylbenzene was used as an internal standard, and the results were corrected for differences in detector response.

Solutions of pyrene and phenanthrene with tetralin do not react in neat $SbCl_3$ at 80°C. Only the NMR spectra of the parent PAH and tetralin are observed even at temperatures up to 130°C. However, anthracene and naphthacene react rapidly with tetralin at 80°C, and are selectively hydrogenated to 9,10-dihydroanthracene (DHA) and 5,12-dihydronaphthacene (DHN) respectively. DHA and DHN were identified from a comparison of their ^1H NMR spectra with those of authentic samples (4).

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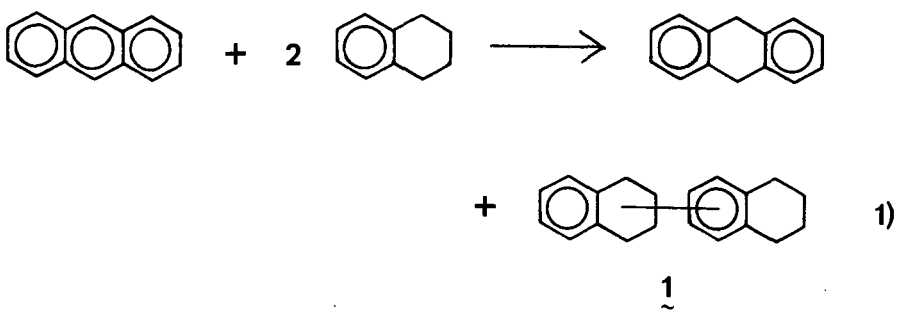
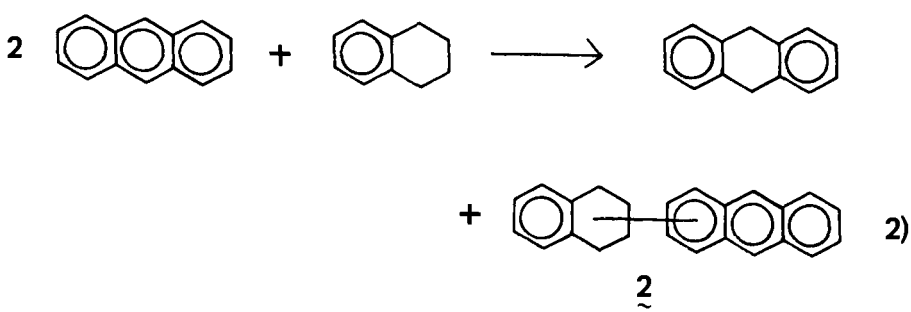
The reaction of anthracene with tetralin in $SbCl_3$ is currently the most extensively studied. Tetralin itself is unreactive in $SbCl_3$ (80-130°C), and anthracene also does not show any reaction in $SbCl_3$ at 80°C for the 30 min reaction period. At longer reaction periods, anthracene slowly undergoes Scholl condensation reactions that we have previously reported (4). This Scholl reaction is believed to proceed through the anthracene radical cation. In the presence of tetralin, however, anthracene does not undergo Scholl condensation but instead is rapidly hydrogenated by tetralin. ^1H NMR experiments using fully deuterated anthracene demonstrate that the hydrogens added at the 9 and 10 positions of anthracene (δ3.99) are from the tetralin. This observation is supported by the quantitative analysis of tetralin, anthracene, and DHA in the organic products from larger scale reactions.

The product distribution and reaction stoichiometry are found to depend on the amount of tetralin initially present. We find that the yield of DHA increases with increasing amounts of tetralin and reaches a maximum of 39% at a 2:1 tetralin: anthracene mole ratio (Table 1). Furthermore, we find from GC-MS that the dehydrogenated tetralin does not produce naphthalene. Instead it forms principally two condensed products 1 (MW = 262) and 2 (MW = 308) whose relative amounts also depend on the initial amount of tetralin present as shown in Table 1. The overall reaction stoichiometry can be described as the sum of two limiting equations with Equation 1 predominating at high tetralin/anthracene mole ratios and Equation 2 predominating at low tetralin/anthracene mole ratios.



1)



2)

We are in the process of determining the structures of 1 and 2, and these results should provide useful clues towards understanding the reaction mechanism.

Although anthracene and naphthacene are hydrogenated by tetralin in $SbCl_3$, phenanthrene and pyrene are unreactive. From a previous ESR study (7) we know that phenanthrene and pyrene are not oxidized by $SbCl_3$ to radical cations, whereas the more easily oxidized PAH's, anthracene and naphthacene, do form radical cations in $SbCl_3$. These results, along with our previous observations of redox driven reactions in $SbCl_3$ in which Sb^{3+} acts as an oxidant (4-6), suggest that the unusual low temperature hydrogenation reactions reported here proceed via reaction of the PAH radical cation with tetralin. Research in this area is continuing in an effort to further elucidate the reaction mechanism.

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Table 1. Influence of Tetralin Concentration on the Anthracene-Tetralin-$SbCl_3$ Reaction[a]

Tetralin (mmol)	Anthracene (mmol)	DHA yield (%)[b]	1/2 mole ratio[c]
0	1.40	0	—
0.70	1.40	20	.15
1.40	1.40	30	.50
2.80	1.40	39	1.5
5.60	1.40	38	3.5

[a]Reactions were run in 34.2 mmol $SbCl_3$ at 80°C for 30 min.

[b]Based on original anthracene (±2%).

[c]Based only on gc area ratios.