

BIARYL FORMATION AS A SOURCE OF HYDROGEN DURING PYROLYSIS OF RESID STRUCTURAL ELEMENTS

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ABSTRACT

The problems of formation of carbonaceous solids ("coke") during the processing of heavy petroleum and coal are clearly related to the formation of "excess" alkanes during hydrous or "confined" pyrolysis: in both cases the hydrogen needed to keep the ratio of alkanes/olefins high in the converted (i.e., volatile) aliphatic portions of the product streams must come primarily from the aromatic, or non-volatile, portions of the feed. In the first case, this transfer is undesirable because it forms coke; in the second case, it is (or "was") desirable because it increased the volatility and aliphatic nature of the petroleum pool during source rock maturation. In both cases, we have speculated that the formation of aryl-aryl coupling products is very likely a key step. In an effort to connect the dominant chemistry in these two contexts, we are performing experimental and mechanistic numerical model studies on selected structures as surrogates for the petroleum resid and kerogen components as well. One question of interest is how the presence of water in hydrous pyrolysis promotes the critical hydrogen transfer, particularly since the 118-kcal/mol O-H bond in water makes it very difficult for water to participate in any radical-chain hydrogen transfer pathways. Initial results are in accord with this reservation in that the presence of supercritical water, up to a fluid density of 0.4 g/cc, did not enhance the redistribution of hydrogen to produce more volatile alkanes.

INTRODUCTION

Hydrogen redistribution among feedstock components or structural elements is key to both the conversion of vacuum resids to distillate materials, and also to the formation of volatile fractions during hydrous pyrolysis. In the case of resid hydroprocessing, there is a well-appreciated tendency for some of the hydrogen required for bond scission and radical-capping to come from coke intermediates, thus propelling the formation of coke. This tendency toward disproportionation is well understood in thermodynamic terms, being due to the respective stabilities of methane and graphite. However, it is poorly understood in terms of the kinetic factors controlling its rate. The goal in catalytic hydroprocessing of resids is of course to ameliorate this tendency to the maximum extent practical through the use of catalysts and hydrogen pressure.

Hydrous pyrolysis of oil shale and other types of kerogen is presumably driven by a similar tendency for the kerogen structure to disproportionate into a hydrogen-rich volatile portion and a hydrogen-poor less-volatile portion. The presence of liquid phase (or dense supercritical fluid phase) water during the hydrous- or confined- pyrolysis is known to markedly increase the alkane/alkene ratio in the volatile products.¹⁻³ Since the evidence appears to indicate that water does not serve as the principal source of additional hydrogen in the volatile products, the additional hydrogen must be coming, as in the resid hydroprocessing case, from the organic matrix itself. Our basic premise is that the hydrogen-transfer chemistry in these two cases is closely related. Accepting that premise as a working hypothesis, the pertinent question then becomes, "From what structures and by what chemical mechanisms does this hydrogen come, and how might water influence that transfer?"

It is well known that petroleum residua consist basically of large polycyclic aromatic (PAH) clusters to which are attached a number of aliphatic chains. It is also generally appreciated that the problem of resid hydroprocessing is not primarily one of cracking off the alkyl chains, which occurs rather readily (even the absence of H₂ and a catalyst)⁴⁻⁶, but one of doing so without having

the PAH form carbonaceous solids that foul the catalyst, coat reactor surfaces, and build aggregates that interfere with fluid bed operation. Nevertheless, prior to 1989, the open literature contained only one report⁷ of the behavior of long-chain alkylaromatics other than of alkyl benzenes⁸ or alkylpyridines.⁹ On the basis of pyrolysis at high temperatures (ca. 800°C), Billaud et al. concluded that the pyrolysis pathways were independent of the number of rings in the PAH.⁷ However, in work first reported in 1988, Savage and coworkers¹⁰⁻¹² showed that the conclusions of Billaud et al. definitely *do not* apply to pyrolysis at lower temperatures, particularly to the 350-450°C range relevant to resid hydroprocessing and hydrous- or confined- pyrolysis. Their experiments demonstrate very clearly that the ease of bond cleavage at the alkyl-aryl junction (i.e., ipso displacement) depends very markedly on the number and arrangement of rings in the PAH, ranging from extremely slow for alkylbenzenes to very fast for certain pyrenyl, anthryl, chrysyl, and perylenyl derivatives. For these PAH, the ipso displacement is so facile that it is often the dominant reaction in pyrolysis of the neat alkylaromatic (that is, even in the absence of a hydro-aromatic or other "intended" hydrogen-transfer agent). The relative ease of this ipso-displacement is also completely consistent with findings on the relative ease of hydrogen transfer to these same categories of structures under donor-solvent coal liquefaction conditions.¹³⁻¹⁵ The purpose of this presentation is to address the question of where the hydrogen comes from and how it arrives at the ipso position of these alkylaromatics.

EXPERIMENTAL

Procedures. Pyrolysis experiments were carried out in evacuated fused silica ampoules. The sealed tube and an appropriate quantity of solvent for pressure equalization was placed in an outer jacket of stainless steel tubing capped with compression fittings. The reaction vessel was then immersed in a temperature-controlled molten-salt bath for the desired time, the tube removed and quenched in water. After cooling in liquid nitrogen to condense CO₂ and volatile organics, the ampoule was opened and the sample removed by pipet and repeated washing of the tube with solvent. An internal standard was added and the sample analyzed by capillary gas chromatography with flame ionization and/or mass selective detection. Quantitation was obtained using the FID analyses with molar responses determined separately for those compounds for which we had authentic samples and estimated by comparison with similar species when no sample was available. Generally, at least three split injections of each sample were performed using an autoinjector. For most species the reproducibility was within $\pm 2\%$ and we estimate the overall analytical accuracy to be within $\pm 5\%$. The reaction mixtures were also analyzed by field ionization mass spectrometry (FIMS), using SRI's magnetic sector FIMS instrument, in order to assess the polyaryls and other low volatility products.

Chemicals. n-Hexadecylpyrene (99+% by GC analysis), was obtained from Molecular Probes, Inc. of Eugene, Oregon. Biphenyl was obtained from Aldrich Chemical Co. Toluene used for GC analyses was Malinkrodt reagent grade. These materials were used without further purification. Tetrahydrofuran was used without stabilizer and distilled daily from sodium acetylacetonate. The added-water pyrolyses employed deionized, low-conductivity water.

RESULTS

Initial pyrolysis experiments with n-hexadecylpyrene were conducted under conditions similar to those used by Savage and coworkers and the products analyzed by GC-MS and FIMS. Subsequently, we performed some experiments with added (supercritical) water. To facilitate comparison, Table I gives summary figures relating to the balance of hydrogen, and aromatic and aliphatic carbon for the pyrolysis of 1-dodecylpyrene calculated from the data of Savage and coworkers¹¹ along with findings from our study.

Perhaps the most striking observation in these and other data of Savage is the very high alkane/alkene ratio in the reported products, particularly at large extents of reaction. It is also clear from these data there is a shortage (in the GC-MS analyzable products) of pyrene rings and of

hydrogen-deficient materials. Evidently, non-volatile, hydrogen-deficient, pyrene-containing products (aka char) have been generated in the course of converting radicals and olefins (produced from ipso-displacement and Rice-Herzfeld alkyl chain scission) into alkanes. The high alkane/alkene ratio, in the absence of an external source of hydrogen, is strikingly reminiscent of the ratios reported by Lewan¹ and others for hydrous pyrolysis of shale kerogen.

Reaction Rates and Hydrogen Balance. The defined first order rate constant (for alkylpyrene disappearance) from the 90-minute quartz ampoule pyrolysis is only about 1/8 of that obtained by Savage¹¹ in a stainless steel reactor after reaction for the same time. The rate constant derived from the 513-minute run is about three times higher. This increase in first-order rate constant is consistent with the autocatalysis described in reference 11, although it is difficult at this point to precisely compare the degree of autocatalysis in the two reactor types. The product distributions are quite similar, with there again being a marked excess of alkanes over alkenes and a substantial shortage of pyrene-containing products at higher extents of reaction. The extent of this excess and shortage are shown in Table 1. The mol % yield of alkanes is numerically equivalent to the mol % of "extra" hydrogen required to produce cleaved and reduced (non-olefinic) products. As the conversion of the alkylpyrenes approaches 90%, the yield of extra hydrogen in the reduced products can also approach 90%, meaning that out of every ten original alkylpyrenes that have disappeared, there have been nine chain cleavages that have utilized this extra hydrogen coming from somewhere. Savage and coworkers pointed out this hydrogen imbalance,¹¹ but were unable to address with GC-MS the nature of the incipient "char" that was presumably providing the hydrogen.

The last two columns in Table 1 show the products obtained when water was included in the reaction mixture along with the organic substrate (at ca. 0.1 and 0.4 g/cc supercritical fluid density). As indicated above, the question of interest here was whether the addition of water would accelerate the formation of those oxidized products whose generation supplies hydrogen (and therefore accelerates cleavage and reduction). The data in Columns 7 and 8 clearly indicate that this was *not* the case. In fact, there was a consistent and progressive *decrease* in the alkane/alkene ratios seen in the aliphatic products, as reflected by 45 and 80% drops in the overall alkane/alkene ratio shown for the two water runs in Table 1. Thus, the effect of water under these conditions has not only *not* been to increase cleavage and reduction, but to make the volatile products more oxidized (olefinic).

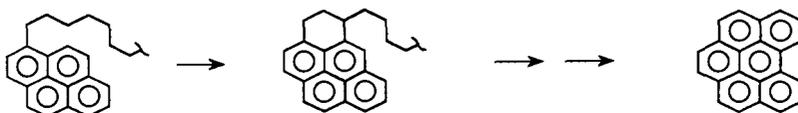
Assuming our originally postulated connection between alkylpyrene pyrolysis and hydrous pyrolysis really does exist, the reason why water failed to accelerate cleavage is likely that here there are virtually no ionic species, other than those provided by the autoionization of the water itself. There is neither the mineral matter, nor the organic heteroatom species, nor the stainless steel surfaces generally present in hydrous pyrolysis of oil shale and other kerogens. In fact, the pyrolysis of alkylpyrenes in fused silica ampoules represents the extreme in terms of a "kerogen surrogate" free from any ionic or polar species that may be contributing to the marked effects that water has in hydrous pyrolysis. It does make sense, after all, that if water as a polar medium and ionic reactant is to somehow help connect the ionic reaction manifold to the radical reaction manifold, this will likely require not only fluid densities approaching normal liquid densities¹⁶ (i.e., above ca. 0.3 g/cc) but also the presence of polar species and redox agents. Accordingly, experiments are now underway to see if any of these factors will enable water to accelerate the redistribution of hydrogen and enhance the production of reduced ipso-displaced products during alkylpyrene pyrolysis.

Identity of the Sources of Extra Hydrogen. Savage describes an acetone-insoluble, toluene-soluble non-elutable "char" as the probable source of the hydrogen that produces high alkane/alkene product ratios. The major elutable unidentified product reported by these workers¹¹ was a material whose presumed molecular ion was reported as m/z 242. Based upon recent field ionization mass spectrometric analyses we have performed on Wilsonville coal liquefaction residues in conjunction with Consolidation Coal Co.¹⁷ and also on earlier HPLC-FIMS analyses of petroleum-resid-derived vacuum gas oils reported by Sullivan et al.,¹⁸ we can identify m/z 242 as the odd-carbon aromatic derived from pyrene by completion of a -CH₂CH₂CH₂- bridge between

the 1- and the 10- positions. As an analog of phenalene ($C_{13}H_{12}$) it is an odd-carbon molecule that would have to lose three hydrogens to be fully aromatic, it cannot form a closed shell fully aromatic PAH. However, the radical species formed when three hydrogens are lost is among the most stable of all radicals, and earlier esr studies have found it to be common in thermally processed petroleum *even at room temperature*.



From our recent analyses of Wilsonville coal-derived resids,¹⁷ it is apparent that m/z 242 is a commonly recurring PAH structure that builds up during catalytic processing. How important it actually is as a step in the ring-growth processes that lead to still larger PAH and eventually char is a critical question, the answer to which has not yet appeared in the literature. However, a partial answer appears here in the form of a second important higher molecular weight product we have detected. At longer reaction times the molar yield of this product approaches 3%, and, from its apparent molecular ion at m/z 276, this product can be identified as benzo[ghi]perylene. Although not previously reported in alkyl pyrene pyrolysis,¹⁰⁻¹² this PAH has been found to be prominent in coal- and petroleum- derived resids and to be correlated with increased problems of coke formation.¹⁸ Benzoperylene could conceivably be formed from the original 1-alkyl pyrene by two successive ring closures, as shown below, proceeding through an intermediate having the m/z 242 ring system.



Thus it begins to appear that the phenalene-type structure represented by m/z 242 is in fact important in the ring-growth processes by which higher PAH and eventually char are produced. Benzoperylene (m/z 276) represents five degrees of unsaturation beyond pyrene. Taken together with cleavage of the residual alkyl chain, the net result is the freeing of four units of 2(H) for the production of reduced and cleaved products. For the 513 min run in Table 1, the formation of the single product at m/z 276 accounts for a significant minority of the extra hydrogen made available: the yield of benzo[ghi]perylene represents about 11 percentage points of the 85 mol% of 2(H) generated by "char-forming" reactions.

The operation of ring-growth mechanisms that involve attachment and cyclization of alkyl fragments is of course not the only way of generating the larger PAH that eventually become char. The formation of biaryls and their ring-closure (e.g. naphthalene to binaphthyl to perylene) represents passing from pre-existing aromatics to much larger PAH in a minimum number of steps. Furthermore, given that biaryl bonds are the strongest C-C single bonds that can be formed in hydrocarbons, the formation of biaryls can be expected to be very facile *once* aryl radicals have been generated.¹⁹ In contrast, one rather expects that alkylation and cyclization would become much more facile in the presence of acidic catalysts.²⁰ Hence, we expected in these pure hydrocarbon pyrolyses to find biaryls as the major oxidation products.

We subjected one of the product mixtures from ethylpyrene pyrolysis (supplied to us by Savage) to FIMS analysis to assess the formation of biaryls (which are not analyzable by capillary GC). The spectrum from this analysis is presented in Figure 1. Even though the extent of reaction in this case was only about 35% and the yield of pyrene is only about 5%, the peaks for dimers and

trimers of ethylpyrene are clearly visible. In contrast, the peak at m/z 242 is barely above background and there is no peak visible at m/z 276. Thus it would appear that under these nominally non-ionic conditions, biaryl formation is indeed a more important source of hydrogen than alkylation and ring-closure processes.

FIMS analysis of the 513-minute reaction product (sample from Row 6 in Table 1) does not show such clear presence of biaryls, presumably because rather than having dimer intensity primarily at three masses ($2(230) - 2$, $2(230) - 2 + 28$, and $2(230) - 2 - 28$) as in Figure 1, the class of dimers will be distributed over at least 32 different masses (i.e., $m/z = 2(426) - 2$ and any mass containing from one to 32 fewer side chain carbons). However, the ring-building species at m/z 240, 242, and 276, and are clearly visible, together with modest amounts of the corresponding 276-alkylation products up to the C₁₇ analog. These alkylation products of benzoperylene, in sum, essentially double to about 20 percentage points the extra hydrogen supplied through the formation of all benzo[ghi]perylene species. Thus, both biaryl formation and ring-building processes can each be seen, under different circumstances, to supply substantial percentages of the hydrogen used for ring closure and olefin reduction.

SUMMARY

Pyrolysis of long chain alkylpyrenes at 400°C in fused silica ampoules yields a product distribution and autocatalytic behavior very similar to that detailed by Savage for reaction in stainless steel microreactors, but at about an 8-fold lower rate. The hydrogen needed for the ipso-displacement bond cleavage and for reduction of olefinic products is indeed supplied by the generation of heavy materials. From GC-MS and FIMS analysis, we find both ring-growth and poly-aryl products to be significant sources of this "extra" hydrogen. Some of these ring-growth products, particularly the odd-carbon phenalene analog at m/z 242 and benzo(g,h,i)perylene at m/z 276 have been previously correlated with buildup of coke and refractory resids during catalytic hydroprocessing of heavy petroleum and coal-derived liquids. Somewhat surprisingly, we do *not* find that the addition of supercritical water, at least up to a fluid density of 0.4 g/cc, enhances the formation of biaryls and thereby enhances this supply of extra hydrogen. This observation leads to the tentative conclusion that the interaction of water and the organic matrix that commonly leads to an enrichment in volatile hydrocarbons during hydrous pyrolysis must depend upon the presence of ionic or polar species that are not present during pure hydrocarbon pyrolyses in fused silica. We anticipate that extension of these studies will yield important information on factors controlling coke formation during processing of residual oils as well as on the chemistry responsible for alkane enrichment during hydrous pyrolysis.

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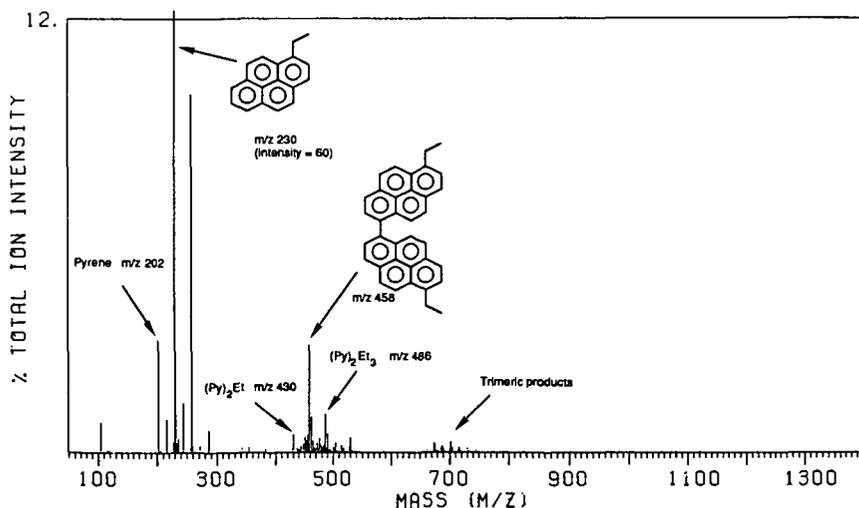


Figure 1. Mass spectrum of a moderate-conversion 1-ethylpyrene pyrolysis product mixture.

Table 1

Comparison of literature and current data on the pyrolysis of long chain alkyipyrenes.

	Literature Data ^a			Current Results ^b			
	30	90	180	90	513	90	90
Time (min)	30	90	180	90	513	90	90
Water density (g/cc)	-	-	-	-	-	0.12	0.40
10 ⁴ Defined k ₁ (s ⁻¹)	1.39	1.84	2.62	0.24	0.60	0.25	0.31
Products (mol%)							
Pyrene	0.74	20.7	43.5	1.91	52.9	1.41	0.28
Me-Pyrene	2.86	6.62	8.38	5.47	9.64	6.04	6.19
Et-Pyrene	1.90	2.08	2.68	1.55	2.35	2.64	1.50
Vinyl-Pyrene	c	c	c	0.033	<0.02	0.14	1.96
Σ(Pyrenes)	82.6	71.9	65.8	Unk	Unk	Unk	Unk
Σ(Identified Pyrene Products)	4.8	34.8	59.9	11.9 ^d	80.3 ^d	12.4 ^d	15.4 ^e
Σ(Alkanes) ^{f,g}	>1.94	>23.5	>54.9	>6.49	>85.14	>5.34	>2.19
Σ(Alkenes) ^f	>2.37	4.60	>2.61	>4.47	>0.66	>6.74	7.66
Alkanes/Alkenes	0.81	4.60	19.5	1.45	128	0.79	0.29
Excess mols of 2(H) ^g	1.0	24.0	52.3	3.5	77.7	1.9	1.14

a Pyrolysis of 1-dodecylpyrene/biphenyl mixtures at 400°C in stainless steel reactors, Ref. 11.

b Pyrolysis of 1-hexadecylpyrene/biphenyl mixtures at 400°C in quartz ampoules.

c Not reported but stated to be very small due to rapid hydrogenation to ethylpyrene.

d Includes pyrenes with alkyl chain lengths up to C₁₂ and selected ring-closure products.e Includes pyrenes with alkyl chain lengths up to C₁₅ and selected ring-closure products.f Includes aliphatic products from C₈ to C₁₆.

g The mol % yield of alkanes is numerically equivalent to the mol % of excess hydrogen required to produce cleaved non-olefinic products