

ANOMALOUS SIDE CHAIN CLEAVAGE IN ALKYLAROMATIC PYROLYSIS

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INTRODUCTION

In reactions of hydrocarbons, alkylaromatic side chain cleavage occurs as the result of thermal or acid catalyzed cracking chemistry. In general, acid catalysis leads to direct bond cleavage at the aromatic ring whereas thermally promoted bond breaking gives primarily substituted aromatics.¹ The formation of a core aromatic by a thermal process is expected only at higher temperatures and in low yield due to the need for hydrogen atoms.

The thermal chemistry of simple alkyl substituted aromatics has been extensively studied both experimentally² and mechanistically³ over a wide range of temperatures in the gas and liquid phase. Selectivity and conversion can generally be explained by the classical Rice-Hertzfeld chain mechanism,⁴ involving initiation, chain propagation and termination steps.

Typically, thermal cleavage of an alkyl group at the ring for most systems studied (1 and 2 ring alkylaromatics) is observed only at relatively high temperature. It occurs by ipso hydrogen atom attack followed by cleavage and rearomatization by loss of the alkyl side chain.⁵

Recently, for the alkylpyrene system, extensive direct side chain cleavage has been observed for liquid phase, low temperature (375-425°C) pyrolysis (43% yield of pyrene at 400°C and 180 min.).⁶ Pyrene formation was reported to be the result of autocatalysis. This yield of core aromatic is much greater than that found for single ring aromatics.² Detailed mechanistic interpretation of this work is obscured by the high levels of conversion and formation of higher molecular weight residues.

In this paper, we wish to report the results of a combined theoretical and experimental study which we believe does provide experimental confirmation of a direct cleavage path. In support of this conclusion, we present an analysis of the possible reaction pathways.

EXPERIMENTAL SECTION

The model compound used in the pyrolysis studies, 1,20-di(1-pyrenyl)icosane (1) was obtained from Molecular Probes Inc., Eugene, Oregon and used without further purification. The material was 99 % pure by high temperature gc.

Nuclear Magnetic Resonance spectra were recorded using a Brüker AM-360. Peak positions were referenced to tetramethylsilane (TMS) and all spectra were run in CDCl₃. Products were analyzed by gc using either a HP 5890 equipped with an FID detector (column 30M x 0.32mm I.D. SPB-5, cross-linked methyl silicone, 0.25µ) operated in the splitless mode or a Carlo Erba HT SIM-DIST (high temperature simulated distillation) GC. Mass spectral analyses were conducted using an HP5995 GC/MS with RTE-6 Data Station equipped with a column identical to that described above for the HP5890.

A Perkin Elmer TGS-2 Thermogravimetric System was modified and operated to achieve heatup rates up to 20 times faster than it was designed for. The reactor and balance mechanism were enclosed and continuously purged with helium. The TGA thermocouple was calibrated using high temperature Curie Point metals as recommended by Perkin Elmer.

Flash Pyrolysis studies were carried out using a commercial pyroprobe instrument (Chemical Data Systems, Inc. CDS 122 Pyroprobe) equipped with an electrically heated platinum coil on the end of an

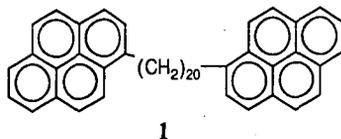
insulated probe. In a typical experiment, the nonvolatile model compound of interest was coated on the wire by placing a small amount of the organic material onto the coil and then heating until the material melts and formed a thin film on the surface. The probe was then fitted with a glass tube sealed at one end, and the pyrolysis chamber was purged with helium. The coil was then rapidly heated to temperature (600 to 1000°C max.) at the maximum rate possible (nominally 20,000 °C per sec) and maintained at temperature for the desired reaction time. Products collected on the inside surface of the air cooled tube and were washed down the tube with solvent and analyzed by gc, gc/ms, and ¹H NMR spectroscopy.

A detailed chemical kinetic model for the pyrolysis of **1** was constructed using an abbreviated set of reactions from the modeling of butylbenzene.³ The thermochemistry was changed to reflect the increased stability of the 4-ring benzylic like radical relative to the one ring case. Stein and Golden estimate this to be 8 kcal/mole.⁷

RESULTS AND DISCUSSION

Pyrolysis Experiments

We have conducted pyrolyses using open reactor configurations and flash pyrolysis methods. The model used was 1,20-di(1-pyrenyl)eicosane (**1**) (bp. ~620°C, estimated from gc simulated distillation).



When **1** was pyrolyzed in an open reactor (TGA) at 425 and 512°C, the sample weight loss was monitored as a function of time. The products were collected and analyzed by high temperature GC. Liquid product recovery was nearly quantitative (99%) plus a 3% yield of a nonvolatile residue (total mass recovery 102 %) for the 425°C sample. For the 512°C sample, liquid and residue yield were 94 and 2% respectively (total mass recovery 96%).

GC results show some starting material in the volatile liquids (32 % at 427 °C and 9 % at 512°C) and the formation of a substantial amount of pyrene and its paired pyrolysis product, 1-eicosylpyrene as well as the usual series of paired alkyl and terminal alkenylaromatics. This confirms the importance of an anomalous direct side chain cleavage pathway in alkylpyrene pyrolysis. It also indicates the extent of volatilization of **1** under the TGA experimental conditions.

In figures 1a and b, a schematic representation of the product selectivity data is given for the 427 and 512 °C runs. The plots clearly show the general pairing of products when an internal carbon-carbon bond is cleaved. Comparison of the plots demonstrates the suppression of pyrene production at high temperature. This is consistent with the sealed tube data in reference 6. Table I quantifies these trends for the alkylpyrenes, includes flash pyrolysis data for **1** at 575°C, and includes product selectivities for butylbenzene at 505°C for comparison.

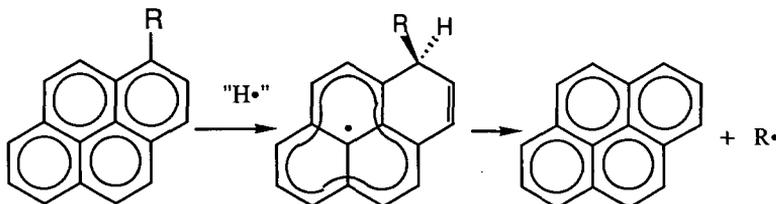
The proton NMR spectrum for the products derived from flash pyrolysis at 425°C is shown in figure 2 with an enlargement of the olefin region. The four multiplets on the right of this region are unambiguously assigned to the terminal hydrogens of vinylpyrene and the olefinic hydrogens of the series of terminal olefins (chain length greater than C₂) substituted on pyrene.⁸ The downfield multiplet is assigned to the beta hydrogen of an alkyl substituted vinylpyrene (see fig. 2b). Its chemical shift and coupling pattern are consistent with the trans isomer. Figure 2b shows a comparison of the experimentally observed adsorption and a spectral simulation.⁹ Using standard literature coupling constants,¹⁰ excellent agreement is obtained.

Formation of the internal olefin discussed above provides a candidate for the missing source of hydrogen needed for side chain cleavage. Confirming support for this hypothesis was obtained by tracking the formation of this species relative to pyrene at different temperatures. The ratios for pyrene to vinylpyrene and internal olefin to vinylpyrene are 0.46 and 0.41 (575°C max.) and 0.24 and 0.21 (800°C max.)

respectively.¹¹ These values clearly show that formation of the internal olefin is coupled to pyrene formation.

Mechanistic Interpretations

In the general case, three mechanistic possibilities exist for the conversion of an alkylpyrene to pyrene and an alkane. They are distinguished by the following elementary reaction features: 1) ipso hydrogen atom addition, 2) bimolecular radical hydrogen transfer, RHT (transfer of hydrogen from a location beta or, in the general case, distant from the site of highest spin density at alternate carbons),^{12,13} and 3) a multistep path with internal hydrogen transfer. All are assumed to involve the intermediacy of an adduct formed from the addition of a hydrogen atom to position 1 of the 1-substituted pyrene. The resulting species from this addition is a very stable polycyclic aromatic π -radical and is formally a vinyl substituted perinaphthyl radical (2). It is also expected that this intermediate will fragment rapidly to give the parent pyrene and an alkyl radical. The critical mechanistic steps concern the formation of 2.



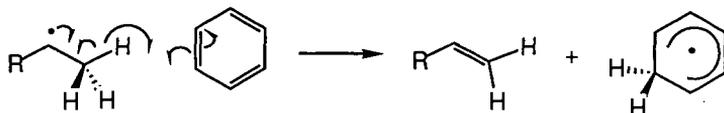
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Ipsa Hydrogen Atom Addition

The production of pyrene and n-C₂₀-pyrene decrease with increasing temperature. Previous experimental and modeling results on butylbenzene show an increase in benzene production by ipso hydrogen atom addition with increasing temperature. Kinetic modeling results in this work also show that an ipso hydrogen atom addition would yield an increase in side chain cleavage with increasing temperature. Since the experimental results are opposite this trend, we believe that free hydrogen atoms are not the primary cause of the cleavage.

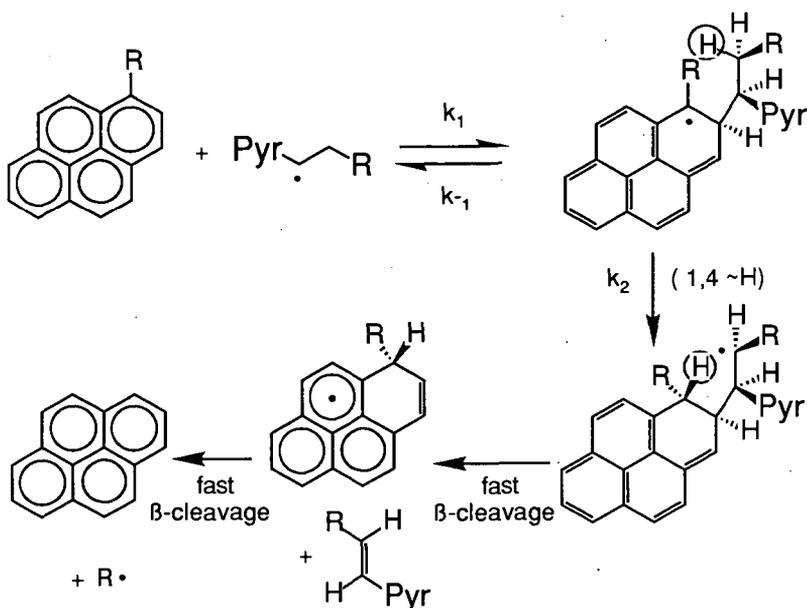
Radical Hydrogen Transfer (RHT)

Examination of the radical hydrogen transfer pathway from a thermochemical kinetic perspective requires a knowledge of the intrinsic reaction barriers and the heats of formation of the intermediates. For the proposed direct radical hydrogen transfer mechanism, little information exists concerning the barrier heights for this process.



An estimate of the barrier for radical hydrogen atom transfer (RHT) can be calculated from literature rate constants for a nearly degenerate case ($\Delta H = 0$) involving transfer of hydrogen from a 2-ethyl-9-hydroanthryl to anthracene.¹⁴ Using a typical bimolecular pre-exponential factor, an E_a value of 18 kcal/mol is obtained.

From the above discussion, a key piece of information required to assess the viability of RHT as a mechanistic alternative is a quantitative estimate of the pyrene-derived vinylperinaphthyl radical stabilization energy. Estimates of hydrogen atom addition heats to a series of polycyclic aromatic systems have been reported. Unfortunately, large disagreement exists for the pyrenyl and phenanthryl ring systems. For perinaphthyl radical, estimates of resonance stabilization range from 22 to 47 kcal/mole



We estimate that the reaction enthalpy for addition and for the subsequent hydrogen transfer to be quite endothermic (~ 24 and 14 kcal/mole, respectively). Using a steady state analysis of the initial addition adduct and typical intrinsic barriers with these reaction enthalpies leads to a product production rate which is many orders of magnitude less than the observed rate constant for pyrene formation extracted from kinetic modeling. Hence, no multistep mechanism that we can envision competes with the remote hydrogen transfer pathway.

CONCLUSION

From our experimental work and modeling, we conclude that alkylpyrene side chain cleavage at the aromatic ring is unusual in two ways: First, it involves the specific structure of the pyrene system in that ipso addition of a radical generates a highly stable vinyl perinaphthyl radical and second, the critical, perinaphthyl like, intermediate is formed by a remote hydrogen transfer reaction. We estimated the heat of formation of the critical intermediate described above, and this supports a perinaphthyl radical stability of 47 kcal/mole, which is at the high end of literature values.

Product studies have revealed the formation of an internal olefin conjugated to pyrene during pyrolysis of model alkylpyrene which is produced in concert with pyrene. This provides confirming evidence for the source of hydrogen needed to effect bond cleavage. This information plus thermochemical analysis limits the mechanistic possibilities to a process that must involve direct bimolecular radical hydrogen transfer.

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8. ¹H NMR: Vinylpyrene terminal olefins (trans H, 5.98 ppm, J_{trans} = 17.4 Hz, J_{gem} = 1.2 Hz; cis H, 5.60 ppm, J_{cis} = 11 Hz, J_{gem} = 1.2 Hz); aliphatic chain olefins (terminal H's, 5.02-4.87 ppm, dd with allylic coupling, non terminal H, 5.79 ppm, multiplet).
9. Brüker spin system simulation software "PANIC", Parameter Adjustment in NMR by Iterative Calculation, 1985 version.
10. Typical coupling values were used in the simulation and gave peak positions and intensities nearly identical with the observed pattern; For the beta vinyl hydrogen in the internal olefin, J_{1,2}(trans olefinic coupling) = 15 Hz, J_{2,3}(olefinic to CH₂) = 5.8 Hz = J_{2,4}; Gorden, A.J., Ford, R. A. *"The Chemist's Companion"*; John Wiley & Sons; New York, **1972**, 269.
11. The pyrene to vinylpyrene ratio was obtained by gas chromatographic analysis while the internal olefin to vinylpyrene ratio was obtained by integration of the olefinic region of the ¹H NMR spectrum (see figure 2).
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Figure 1a: Product Selectivities at 427°C Pyrolysis of 1

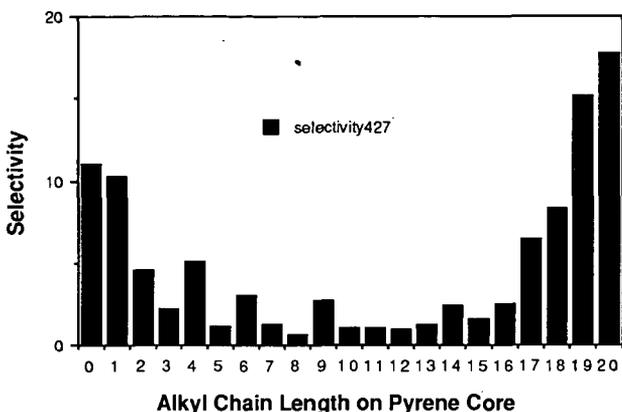


Figure 1b: Product Selectivities at 512°C Pyrolysis of 1

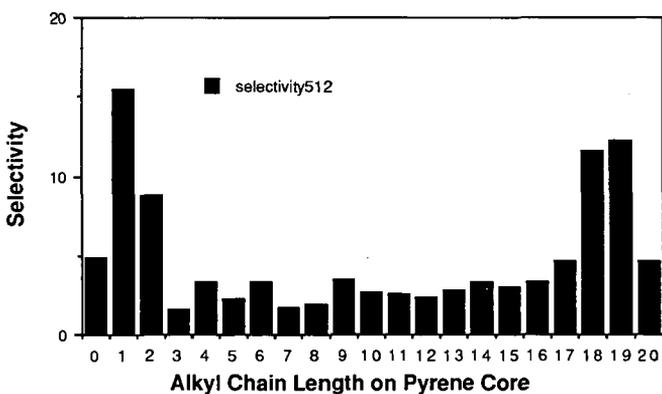


Figure 2a: ^1H NMR Spectrum (360 MHz) of Flash Pyrolysis (575°C max.) with Expansion and Blow-up of Olefinic Region.

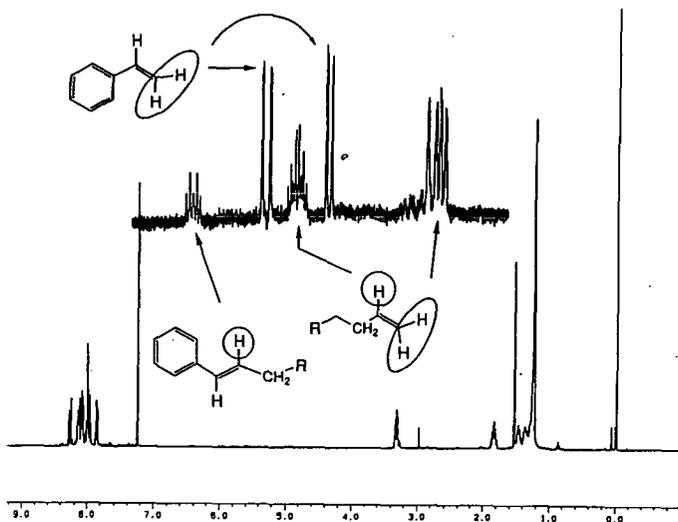


Figure 2b: Comparison of Measured and Simulated Proton NMR Spectrum of H_2 in the Internal Olefin Product.

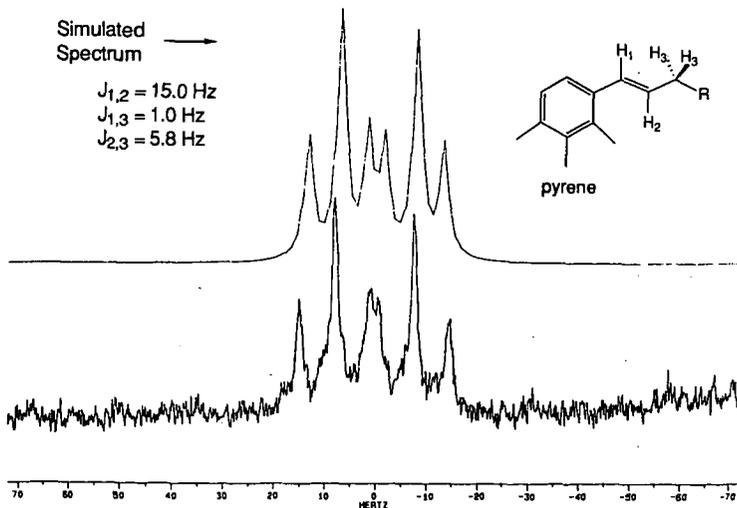


Table 1: Product Selectivities For Sealed Tubes (Savage et al.), OpenReactor (TGA), and Pt Wire (Flash Pyrolysis) Relative to Methylpyrene. Single Ring Data is for Butylbenzene.

	Savage et al.		TGA		Pt Wire	Single Ring Gas Phase
Pyrene	4.3	2.7	1.1	0.32	0.19	0.05
Methylpyrene	1.0	1.0	1.0	1.0	1.0	1.0
C2-pyrene	0.35	0.55	0.44	0.57	0.54	2.2
Temp. (°C)	375	425	425	510	575	505
Citation	ref. 6		this work		this work	ref. 2a