

Reactions of Polycyclic Alkylaromatics: Structure and Reactivity

C. Michael Smith and Phillip E. Savage

University of Michigan, Dept. of Chemical Engineering, Ann Arbor, MI 48109

A family of alkyl-substituted polycyclic aromatic hydrocarbons was pyrolyzed in microbatch reactors at temperatures between 350°C and 425°C. A general pyrolysis network was deduced for these compounds, and it comprised two major and one minor parallel pathways. The first major pathway resulted in products analogous to the major products observed from alkylbenzene pyrolysis. The second major pathway led to products via the cleavage of the strong aryl-alkyl C-C bond. The third pathway led to small amounts of products, presumably through cyclization and condensation reactions. The relative importance of the two major pathways varied for the different compounds. The rates of aryl-alkyl bond cleavage differed for the different compounds, and these rates were quantitatively related to the compounds' localization energies through Dewar reactivity numbers.

Introduction

Often the catalyst for the development of a novel chemical process or the improvement of an existing process can be an enhanced understanding of the intrinsic chemistry of the system. One approach to elucidating the chemistry of heavy hydrocarbons (for example, coals, heavy oils, and kerogens) involves the selection of and experimentation with simple compounds that serve as models of important reactive moieties within the complex feedstock. This approach, termed chemical modeling, has been implemented successfully in the past to provide insight into the reaction fundamentals of coals (Poutsma, 1990; Squire et al., 1986; Gavalas et al., 1981), lignins (McDermott et al., 1990; Train and Klein, 1988), and petroleum asphaltenes (Savage and Klein, 1989a; Neurock et al., 1989; Hikita et al., 1989).

Asphaltenes, the focal point of this study, are defined as the fraction of a crude oil that is insoluble in an aliphatic solvent (such as heptane), but soluble in an aromatic solvent (such as benzene). They are ubiquitous in heavy oils and resids and account for 20% of the weight of these materials. Furthermore, asphaltenes contain high-molecular-weight, condensed aromatic, metals-containing compounds, which lead to many problems (such as rapid catalyst deactivation) in heavy oil processing. These factors have motivated much research into asphaltene reaction pathways, kinetics, and mechanisms.

The current understanding of asphaltene microstructure (Mieville et al., 1989; Ali et al., 1990; Speight, 1988, 1989; Waller et al., 1989; El-Mohamed et al., 1986) indicates that clusters of aromatic rings linked together through aliphatic chains are important structural features. Typical clusters can contain up to six rings, and aliphatic chains can contain from 1 to 20 carbon atoms. Thus, *n*-alkylaromatic compounds are relevant chemical models of the hydrocarbon portion of petroleum asphaltenes.

The pyrolysis of *n*-alkylbenzenes, the simplest compounds in this class, has been extensively investigated (Mushrush and Hazlett, 1984; Blouri et al., 1985; Savage and Klein, 1987a,b; Freund and Olmstead, 1989). The results of these works showed that the alkylbenzene pyrolysis network involves free-radical chemistry and leads to three product lumps. For example, the pyrolysis pathway for *n*-pentadecylbenzene (PDB) leads to toluene and 1-tetradecene as a product pair, styrene and tridecane as a second pair, and a series of alkylbenzenes, alkenylbenzenes, *n*-alkanes, and α -olefins in much lower yields as the third product lump (Savage and Klein, 1987a). The first of these product pairs results from the facile β -scission of the γ -pentadecylbenzene radical, which yields a resonance-stabilized benzyl radical and 1-tetradecene. The second major product pair, styrene and tridecane, is formed through the fastest hydrogen abstraction step and attacks the α -position in pentadecylbenzene. Numerous minor products are formed through β -scission and hydrogen abstraction steps with similar kinetics, so they are lumped collectively into a third product group.

Correspondence concerning this article should be addressed to P. E. Savage.









Model Compounds	Name	Alkyl Chain Length	Dewar Number
	DDB	12	2.31
	BN	4	2.12
	UDN,DDN	11,12	1.81
	DDH	12	2.18
	DDA	12	1.26
	OC	8	1.67
	DDP	1-16	1.51
	HP	6	1.33

Figure 1. Petroleum asphaltene model compounds.

Although the pyrolysis of *n*-alkylbenzenes is now well understood, much less is known about the pyrolysis of polycyclic *n*-alkylaromatics. Recent pyrolyses of *n*-alkylpyrenes, however, have revealed that the pyrolysis network for alkylbenzenes does not completely describe the pyrolysis pathways for these polycyclic alkylaromatics (Smith and Savage, 1991a,b; Savage et al., 1989; Freund et al., 1990). The pyrolysis of 1-dodecylpyrene (DDP), for instance, led to three product lumps analogous to those observed from alkylbenzene pyrolysis (for example, methylpyrene plus 1-undecene, vinylpyrene plus decane, and a series of alkylpyrenes, alkenylpyrenes, alkenes, and alkanes) plus an additional major product pair, pyrene and dodecane. These latter two products can be formed only through cleavage of the aryl-alkyl C-C bond, and their presence indicates the existence of a new pyrolysis pathway for 1-dodecylpyrene. The presence of this pathway, which was insignificant in alkylbenzene pyrolyses, was unexpected because the C-C aryl-alkyl bond is the strongest in the alkyl chain, and its bond dissociation energy is about 100 kcal/mol (McMillen and Golden, 1982).

This work was motivated by the marked differences that exist between the pyrolysis pathways and kinetics for alkylbenzenes and alkylpyrenes and the relevance of such compounds as chemical models for asphaltenes and heavy crude oils. We sought to determine the effects of the structure of the *n*-alkylaromatic on the reaction pathways and kinetics. The specific variables of interest were: (1) the number of aromatic rings; (2) the configuration of the aromatic rings (kata- or pericondensed); (3) the position at which the aliphatic substituent resides upon the aromatic nucleus; and (4) the length of the alkyl chain. Accordingly, we have pyrolyzed a set of 15 different *n*-alkyl aromatics, as shown in Figure 1. The number

of rings ranged from 1 to 5, and the alkyl chain length ranged from 1 to 16. This article provides the results of our experiments, as well as their implications in terms of a general pyrolysis network for *n*-alkylaromatics and a correlation of the compounds' structures and reactivities.

Experimental Studies

The pyrolyses of the model compounds in Figure 1 were conducted in microbatch reactors neat and in some instances in a benzene diluent. Batch holding times ranged up to 500 minutes, and the reaction temperatures were between 350°C and 425°C.

Materials

All of the model compounds in Figure 1 were available in high purity from commercial sources except for 1-*n*-dodecyl-naphthalene (DDN), which was obtained in 99% purity through a custom synthesis by American Tokyo Kasei. 2-*n*-Dodecyl-phenanthrene (DDH), 1-*n*-undecylnaphthalene (UDN), 9-*n*-dodecylantracene (DDA), 6-*n*-octylchrysene (OC), and 3-*n*-hexylperylene (HP) were obtained from the American Petroleum Institute Project 42 through the Thermodynamic Research Center at Texas A&M University. 2-*n*-Butylnaphthalene (BN) was obtained from the American Petroleum Institute Standard Reference Materials through Carnegie Mellon University. 1-*n*-Dodecylpyrene (DDP) and all the other alkylpyrenes were obtained from either Molecular Probes, Texas A&M University, or Carnegie Mellon University. Dodecylbenzene (DDB), biphenyl, and benzene were obtained from Aldrich.

All pyrolyses were conducted in constant-volume, 316 stainless steel, microbatch reactors. The reactors were constructed from one Swagelok port connector and two Swagelok end caps, and they had a nominal volume 0.6 mL. The reactors were routinely cleaned between experiments by soaking them in a 10% HNO₃ solution and then rinsing them with water and then acetone. Previous work (Savage et al., 1989) established that neither the cleaning procedure nor the reactor material altered the experimental results.

Procedure

The batch reactors were typically loaded with 10 mg of the model compound and 10 mg of an internal standard (such as biphenyl). An inert reaction environment was provided by purging the reactors with argon before closing. After being loaded and closed, the reactors were placed in an isothermal fluidized bath of fine aluminum oxide particles at the desired pyrolysis temperature. Upon reaching the desired holding time, the reactors were removed from the fluidized bath, and the reaction was quenched by placing the reactors in an ambient temperature water bath. The reactors were then opened, and the products were recovered by repeated extraction with benzene.

Analytical methods

The reaction products were analyzed routinely by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). The GC analysis used a Hewlett Packard (HP) model 5890 instrument equipped with a HP 3392A integrator, a flame ionization detector (FID), and a HP 7673A autosam-

Table 1. Product Molar Yields from 1-Undecylnaphthalene Pyrolysis

Pyrolysis Temp. (°C)	375	375	375	375	400	400	400	400	425	425	425	425
Time (min)	20	200	300	400	20	60	145	190	10	60	90	170
Nonane	0.040	0.034	0.050	0.073	0.005	0.017	0.006	0.048	0.010	0.056	0.065	0.087
Decene	0.035	0.082	0.098	0.11	0.013	0.035	0.038	0.038	0.024	0.049	0.035	0.011
Decane	0.005	0.013	0.022	0.039	0.000	0.003	0.016	0.027	0.000	0.022	0.034	0.063
Undecane	0.000	0.013	0.024	0.043	0.000	0.004	0.014	0.019	0.000	0.015	0.024	0.045
Naphthalene	0.000	0.017	0.029	0.053	0.000	0.005	0.016	0.022	0.000	0.020	0.037	0.086
Methylnaphthalene	0.045	0.13	0.19	0.25	0.018	0.054	0.11	0.14	0.034	0.17	0.22	0.28
Ethyl-naphthalene	0.006	0.031	0.047	0.071	0.003	0.017	0.039	0.047	0.007	0.073	0.094	0.12
Vinylnaphthalene	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.006	0.000	0.000	0.000
Undecylnaphthalene	1.0	0.90	0.87	0.83	1.0	0.84	0.69	0.56	0.92	0.50	0.33	0.13

pler. We used both a 5 m × 0.53 mm × 2.55 μm film thickness HP-1 methyl silicone capillary column and a 12 m × 0.12 mm × 0.33 μm film thickness HP-5 (crosslinked 5% phenyl methyl silicone) capillary column for product separation. The GC-MS system included a HP 5890 Series II GC, a HP 5970 mass spectrometric detector, and the HP 59940 MS Chemstation. Products with molecular weights less than octane were not analyzed because they either co-eluted with the solvent or were highly volatile (such as permanent gases). A number of the pyrolysis experiments produced a dark, solid, benzene-insoluble material, which we did not quantify because of the very small amount of model compound used. The correspondingly small gas yields produced also precluded the analysis of the gaseous products.

The reaction products were identified by matching their GC retention times with those of authentic standards and by inspecting their mass spectra. Product molar yields, calculated as the number of moles of product formed divided by the number of moles of the reactant initially loaded to the reactor, were obtained from the GC analyses using experimentally determined FID response factors. Further analytical details have been given by Smith and Savage (1991a,b).

Results

In the following section, we provide the results of the neat pyrolyses of UDN, BN, DDH, DDA, OC and HP. Tables 1

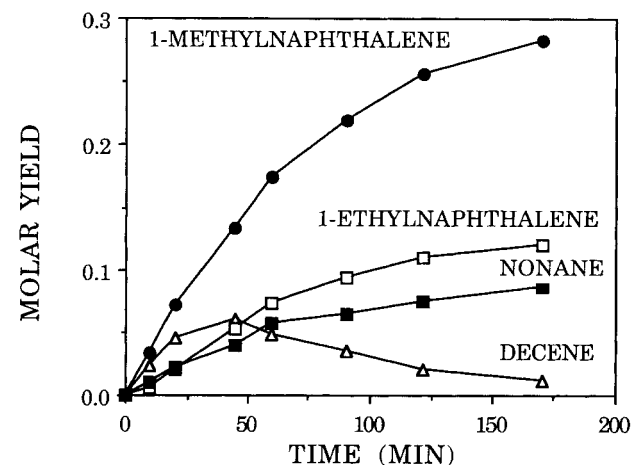


Figure 2. Temporal variation of product molar yields from UDN neat pyrolysis at 425°C

through 6 present representative data in terms of the yields of the major products and selected minor products.

1-Undecylnaphthalene (UDN)

The neat pyrolysis of UDN was conducted at 375°C, 400°C, and 425°C for batch holding times up to 400 minutes. Table 1 provides representative experimental data obtained under a variety of different reaction conditions. The most abundant products at low conversions were 1-methylnaphthalene, 1-ethyl-naphthalene, decene, and nonane. Less abundant products and those formed at higher conversions included decane, naphthalene, undecane, tetrahydrophenanthrene, phenanthrene, and a series of 1-naphthylalkanes and naphthylolefins with alkyl chains containing 3-10 carbon atoms. Of special interest among these minor products were undecane and naphthalene. These products were not present at the shortest batch holding times, but at long times they became major products. For instance, pyrolysis at 425°C for 170 minutes resulted in molar yields of naphthalene and undecane of 0.086 and 0.045, respectively. Note that the formation of this product pair requires the cleavage of the strong aryl-alkyl C-C bond in UDN.

Figure 2 displays the temporal variations of the major low-conversion products for UDN pyrolysis at 425°C. The molar yields of decene and 1-methylnaphthalene were approximately equal at short batch holding times. For example, at a holding time of 10 minutes the molar yields of 1-methylnaphthalene and decene were 0.034 and 0.024, respectively. The molar yield of decene reached a maximum value of 0.059 at a batch holding time of 45 minutes, and then decreased until it reached its ultimate value of 0.011 at 170 minutes. The molar yield of 1-methylnaphthalene, on the other hand, increased steadily throughout the reaction. It achieved an ultimate value of 0.28 at 170 minutes.

Figure 2 also displays the molar yields of nonane and 1-ethyl-naphthalene from the pyrolysis of UDN at 425°C. Similar to the behavior of the yields of 1-methylnaphthalene and decene, the molar yields of nonane and 1-ethyl-naphthalene were approximately equal at short reaction times. For example, at 10 minutes the molar yields of nonane and 1-ethyl-naphthalene were 0.01 and 0.007, respectively. Both yields also increased with time.

2-Butylnaphthalene (BN)

Table 2, which provides representative data, lists the molar yields of the products from BN pyrolyses at 375, 400 and 425°C. The major products from the BN pyrolysis were 2-

Table 2. Product Molar Yields from 2-Butylnaphthalene Pyrolysis

Pyrolysis Temp. (°C)	375	375	375	375	400	400	400	400	425	425	425	425
Time (min)	31	60	120	287	30	83	152	205	25	45	66	80
Naphthalene	0.001	0.001	0.002	0.004	0.000	0.003	0.005	0.007	0.003	0.005	0.015	0.007
Methylnaphthalene	0.005	0.010	0.018	0.033	0.017	0.037	0.046	0.070	0.041	0.072	0.072	0.092
Vinylnaphthalene	0.001	0.001	0.001	0.001	0.006	0.008	0.010	0.000	0.048	0.011	0.014	0.008
Ethyl-naphthalene	0.003	0.005	0.011	0.027	0.022	0.064	0.11	0.14	0.040	0.13	0.16	0.22
Butylnaphthalene	0.86	0.85	0.83	0.78	0.89	0.82	0.74	0.65	0.79	0.67	0.50	0.53

Table 3. Product Molar Yields from 2-Dodecylphenanthrene Pyrolysis

Pyrolysis Temp. (°C)	375	375	375	375	400	400	400	400	425	425	425	425
Time (min)	10	163	187	210	30	45	95	223	10	30	50	159
Decene	0.000	0.004	0.004	0.004	0.003	0.005	0.008	0.009	0.006	0.010	0.013	0.005
Decane	0.002	0.034	0.030	0.034	0.021	0.029	0.058	0.088	0.036	0.065	0.096	0.11
Undecene	0.005	0.058	0.058	0.049	0.037	0.047	0.081	0.064	0.058	0.087	0.097	0.018
Undecane	0.002	0.006	0.005	0.004	0.005	0.004	0.007	0.029	0.003	0.006	0.014	0.029
Phenanthrene	0.000	0.004	0.003	0.002	0.004	0.005	0.007	0.004	0.004	0.009	0.010	0.011
Methylphenanthrene	0.006	0.075	0.080	0.059	0.043	0.061	0.116	0.151	0.018	0.14	0.21	0.30
Ethylphenanthrene	0.000	0.026	0.030	0.020	0.016	0.026	0.046	0.087	0.000	0.073	0.11	0.16
Vinylphenanthrene	0.001	0.001	0.000	0.002	0.002	0.002	0.003	0.000	0.010	0.003	0.002	0.004
Dodecylphenanthrene	0.77	0.89	0.86	0.53	0.63	0.63	0.47	0.31	0.67	0.33	0.20	0.02

methylnaphthalene and 2-ethylnaphthalene. 2-Vinylnaphthalene and naphthalene were observed as minor products. The molar yields of these minor products were typically less than 0.01, except at 425°C where slightly higher yields were obtained. The highest yield of naphthalene was 0.015, which was obtained from the pyrolysis of BN at 425°C for a batch holding time of 66 minutes.

2-Dodecylphenanthrene (DDH)

The pyrolysis of 2-dodecylphenanthrene (DDH) was conducted at 375, 400, and 425°C for batch holding times ranging up to 223 minutes, and Table 3 provides representative results. The major products from DDH pyrolysis were methylphenanthrene, ethylphenanthrene, undecene, and decane. Products formed in lower yields included undecane, 2-vinylphenanthrene, decene, phenanthrene, chrysene, and a series of alkylphenanthrenes. Of the most interest among these minor

products was the formation of phenanthrene. The highest molar yield of phenanthrene was 0.011, which was obtained from pyrolysis at 425°C and 159 minutes where the conversion of DDH was 0.98. The molar yields of phenanthrene were always much lower than the yields of the major products.

Figure 3 displays the molar yields of five selected reaction products as a function of batch holding time for DDH pyrolysis at 400°C. At low batch holding times the molar yields of undecene and methylphenanthrene were approximately equal. For example, at 30 minutes, the molar yields of methylphenanthrene and undecene were 0.043 and 0.037, respectively. At longer batch holding times, however, the molar yield of undecene reached a maximum value and then decreased whereas the yield of methylphenanthrene increased steadily throughout the reaction.

Figure 3 also displays the temporal variations of the yields of ethylphenanthrene and decane for the pyrolysis of DDH at 400°C. The yields of both compounds increased with time, and the yield of decane was always higher than that of ethylphenanthrene. For example, the molar yields of decane and ethylphenanthrene were 0.021 and 0.016, respectively, at a batch holding time of 30 minutes.

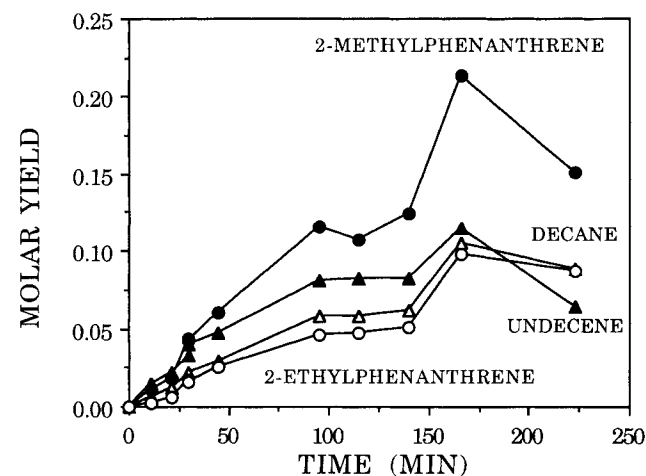


Figure 3. Temporal variation of product molar yields from DDH neat pyrolysis at 400°C

9-Dodecylanthracene (DDA)

The neat pyrolysis of DDA was conducted at 350, 375 and 400°C, and Table 4 provides representative results. The major products from DDA pyrolysis under all conditions studied were anthracene and dodecane. The minor products included decane, decene, undecane, undecene, dodecene, methylanthracene, dihydroanthracene, and tetrahydroanthracene. Of these minor products, dodecene, undecane, and dihydroanthracene had the highest molar yields.

Figure 4 presents the temporal variations of the molar yields of the two major products from the neat pyrolysis of DDA at 400°C. The yields of both anthracene and dodecane increased steadily with time, and the anthracene yield always exceeded the *n*-dodecane yield. The ultimate yields at 40 minutes were 0.71 for anthracene and 0.58 for *n*-dodecane.

Table 4. Product Molar Yields from 9-Dodecylanthracene Pyrolysis

Pyrolysis Temp. (°C)	350	350	350	350	375	375	375	375	400	400	400	400
Time (min)	10	30	90	180	10	20	30	60	10	15	20	40
Decane	0.000	0.000	0.000	0.002	0.000	0.000	0.002	0.006	0.003	0.005	0.009	0.022
Undecene	0.000	0.000	0.000	0.002	0.001	0.000	0.003	0.006	0.006	0.009	0.012	0.000
Undecane	0.000	0.000	0.004	0.011	0.001	0.003	0.005	0.023	0.012	0.015	0.030	0.050
Dodecene	0.000	0.002	0.009	0.019	0.001	0.003	0.010	0.030	0.012	0.017	0.029	0.031
Dodecane	0.005	0.023	0.096	0.25	0.025	0.044	0.11	0.02	0.12	0.19	0.29	0.58
Dihydroanthracene	0.000	0.002	0.003	0.020	0.000	0.003	0.007	0.020	0.003	0.009	0.011	0.079
Anthracene	0.01	0.05	0.17	0.34	0.063	0.10	0.25	0.45	0.19	0.31	0.39	0.71
Methylanthracene	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.007	0.000	0.001	0.000	0.003
Dodecylanthracene	0.71	0.64	0.55	0.04	0.72	0.53	0.26	0.10	0.48	0.28	0.25	0.04

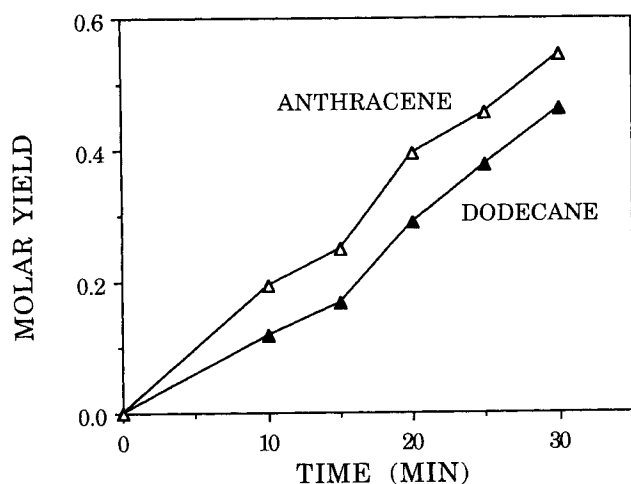
Table 5. Product Molar Yields from 6-Octylchrysene Pyrolysis

Pyrolysis Temp. (°C)	375	375	375	375	400	400	400	400	425	425	425	425
Time (min)	45	215	245	330	15	33	130	180	15	30	45	60
Chrysene	0.000	0.071	0.082	0.074	0.000	0.025	0.13	0.28	0.038	0.12	0.18	0.19
Methylchrysene	0.011	0.047	0.046	0.040	0.016	0.035	0.089	0.12	0.072	0.14	0.17	0.14
Ethylchrysene	0.000	0.020	0.019	0.000	0.000	0.000	0.039	0.039	0.039	0.072	0.076	0.053
Octylchrysene	0.84	0.99	0.79	0.42	0.92	0.90	0.51	0.33	0.92	0.76	0.48	0.19

6-Octylchrysene (OC)

The pyrolysis of OC was conducted at 375, 400 and 425°C for batch holding times ranging up to 330 minutes, and Table 5 lists representative results. The major products were chrysene, methylchrysene, and ethylchrysene. No alkanes or olefins were quantified because these products were either gases or co-eluted with the solvent peak during the GC analysis.

Figure 5 displays the temporal variations of the yields of methylchrysene, ethylchrysene and chrysene for the neat pyrolysis of OC at 425°C. At short batch holding times, the principal product was methylchrysene, and ethylchrysene and chrysene were present in lower yields. As the holding time increased, however, the yield of chrysene increased much more rapidly than did the yields of methylchrysene or ethylchrysene. At a holding time of 40 minutes, chrysene became the major product.

**Figure 4. Temporal variation of product molar yields from DDA neat pyrolysis at 400°C**

3-Hexylperylene (HP)

We conducted the pyrolysis of HP at 375, 400 and 425°C for batch holding times up to 107 minutes, and Table 6 summarizes the experimental results. Perylene was the only product present in yields sufficiently high to quantify. The highest yield of perylene was 0.60, which was obtained at a batch holding time of 30 minutes for the pyrolysis at 425°C. The alkanes and olefins that might have formed from the HP pyrolysis would be C₆ or smaller, and these would have co-eluted with the solvent during the GC analysis or would have been present as gases. Thus, we obtained no data for these alkanes and olefins.

Discussion

Our discussion of the foregoing experimental results will center on three major areas. First, we compare and contrast

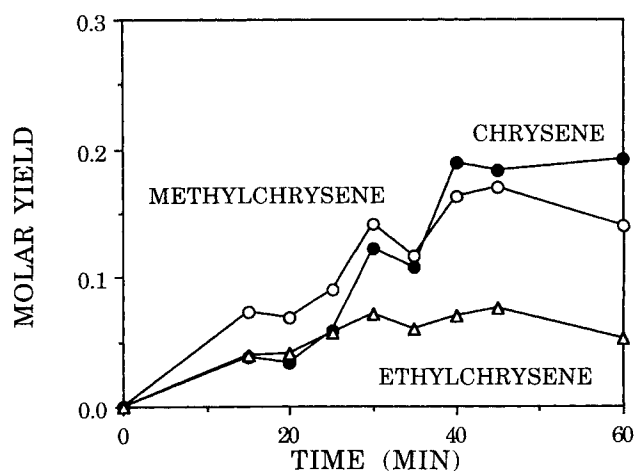
**Figure 5. Temporal variation of product molar yields from OC neat pyrolysis at 425°C**

Table 6. Product Molar Yields from 3-Hexylperylene Pyrolysis

Pyrolysis Temp. (°C)	375	375	375	375	400	400	400	400	425	425	425	425
Time (min)	30	60	92	107	20	30	60	95	10	15	30	45
Perylene	0.11	0.16	0.19	0.24	0.21	0.31	0.60	0.42	0.26	0.23	0.60	0.27
Hexylperylene	0.71	0.49	0.38	0.37	0.72	0.63	0.47	0.14	0.62	0.27	0.21	0.03

the pyrolysis kinetics for each of the model compounds. Secondly, we provide a general reaction network for the pyrolysis of alkylarenes that is consistent with all of our experimental results. Finally, we use perturbation molecular orbital theory to correlate the structures of the compounds with their apparent reactivities.

Pyrolysis kinetics

The results presented in the previous section provide the opportunity to compare and contrast the pyrolysis kinetics for a large number of different polycyclic alkylaromatics. To accomplish this comparison, we calculated pseudo-first-order rate constants for the disappearance of each compound at each temperature investigated. The rate constants for pyrolyses at 400°C and their 90% confidence intervals are shown in Table 7, as well as pseudo-first-order rate constants for the neat pyrolysis of dodecylbenzene and dodecylpyrene. These were calculated from data available in the literature (Savage and Klein, 1987b; Savage et al., 1989a).

Table 7 shows that DDA was the most reactive compound, and DDB, DDH, BN, UDN, and OC were, collectively, the least reactive compounds. DDP and HP were of intermediate reactivity. Thus, for neat pyrolyses at 400°C, the order of reactivity was DDA > HP > DDP > OC ≈ UDN ≈ BN ≈ DDH ≈ DDB. This analysis provides a useful, but perhaps equivocal ranking of reactivity. One reason the ranking is equivocal is that the pyrolysis kinetics are not truly first order. Savage and Klein (1989b), for instance, showed that the reaction order for pentadecylbenzene pyrolysis varied between 1/2 and 3/2 depending on the reaction conditions, and Smith and Savage (1991a) showed that the DDP pyrolysis followed autocatalytic kinetics. Given these complexities in the actual rate laws for *n*-alkylaromatic pyrolysis, however, invoking pseudo-first-order kinetics for this comparison offered a convenient simplification.

Two other reasons that the comparison of the neat pyrolysis kinetics remains equivocal are that the initial concentrations of the compounds were likely different at reaction conditions

Table 7. Pseudo-First-Order Rate Constants (10^3 min^{-1}) for Alkylarene Neat Pyrolysis at 400°C

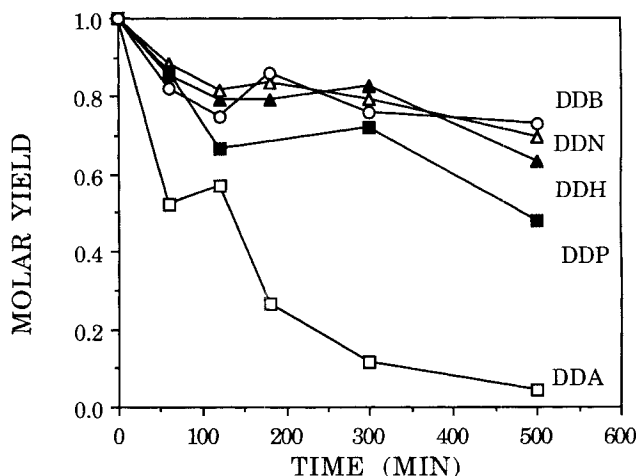
Compound	<i>k</i>	Dewar No.
DDB*	6.4 ± 1.0	2.31
DDH	3.3 ± 1.7	2.18
BN	2.0 ± 0.6	2.12
UDN	2.8 ± 1.3	1.81
OC	5.6 ± 0.1	1.67
DDP**	16 ± 4	1.51
HP	19 ± 9	1.33
DDA	100 ± 26	1.26

*Savage and Klein (1987b)

**Savage et al. (1989)

and that the compounds possessed alkyl chains with different lengths (4 to 12 carbon atoms). The concentrations differed because the compounds had different vapor pressures and liquid densities. The different vapor pressures give rise to different distributions of the reactants in the liquid and vapor phases, and the different liquid densities lead to different liquid-phase concentrations. Our earlier work with DDP (Smith and Savage, 1991a) clearly showed that the initial concentration influenced the kinetics, so these factors may complicate the present comparison. The length of the alkyl chain is also a potential complicating factor because it influences the kinetics of alkylbenzene pyrolysis (Savage and Korotney, 1990).

To assess the importance of the initial concentration and alkyl chain length variations on our reactivity ranking based on neat pyrolysis data, we pyrolyzed a set of five alkylarenes (DDB, DDN, DDH, DDA, and DDP) with identical alkyl chain lengths (12 carbon atoms) at identical initial concentrations (0.02 M) by using benzene as an inert diluent. Figure 6 shows the temporal variations of the molar yields of DDB, DDN, DDH, DDA and DDP from pyrolyses at 400°C. It is evident from Figure 6 that the pyrolysis of DDA is markedly faster than the pyrolysis of DDB, DDN, DDH or DDP. The molar yields of DDB, DDN, DDH and DDP were all similar at short holding times, but at longer holding times the molar yield of DDP was lower than those of the other three compounds. The final reactant molar yield alignment for DDB, DDN, DDH, DDP and DDA at 500 minutes was 0.73, 0.70, 0.63, 0.55 and 0.04, respectively. Thus, there are clear differences between the pyrolysis kinetics for these compounds, and their order of reactivity is consistent with the order obtained from the analysis of the pseudo-first-order rate constants from the neat pyrolyses. Thus, it appears that the small differences in initial con-

**Figure 6. Temporal variation of reactant molar yields from DDB, DDH, DDN, DDP and DDA pyrolysis at 400°C in benzene (0.02 M)**

centration and the different alkyl chain lengths used in the neat pyrolyses did not mask the true relative reactivities of the different compounds.

General pyrolysis pathways

We used two related methodologies to deduce a general reaction network for the pyrolysis of polycyclic *n*-alkylaromatic compounds. Discrimination between primary and secondary products was achieved by examining the variation of: 1. products' molar yields with reactant conversion and 2. products' selectivities with reactant conversion. We used the former approach in our previous alkylarene pyrolysis studies (Smith and Savage, 1991a,b; Savage et al., 1989), and the application of the latter method is illustrated here. This method, termed the Delplot Technique (Bhore et al., 1990), has been used successfully to resolve the reaction pathways for the pyrolysis of pentadecylbenzene (Savage and Klein, 1987a) and phenethyl phenyl ether (Klein and Virk, 1983), and the oxidation of *n*-octane (Garcia-Ochoa et al., 1989). In its simplest form, the Delplot approach permits pathway demarcation through the analysis of the *y*-intercepts of selectivity vs. conversion plots where the selectivity is calculated as the molar yield divided by the reactant conversion. Products that possess nonzero intercepts are of first rank, and those that possess zero intercepts are of higher rank. The rank is the order of appearance of a product within the reaction network (products of first rank are primary products).

The application of this method in Figure 7 shows Delplots for the major products of UDN pyrolysis at 425°C. The curves represent the trends in the data. Figure 7a shows that 1-methylnaphthalene and decene are products of first rank, since extrapolation of their selectivities to zero conversion yields a nonzero intercept. Furthermore, the values of the *y*-intercepts for decene and 1-methylnaphthalene were essentially equal, which suggests that these products were formed in the same reaction step. The selectivity to 1-methylnaphthalene was approximately constant, but the selectivity to decene decreased with conversion suggesting that decene underwent secondary reactions.

Figure 7b is the Delplot for the products vinylnaphthalene, ethylnaphthalene, and nonane. The nonzero and nearly equal intercepts for vinylnaphthalene and nonane reveal that these were products of first rank and that they were formed in the same reaction step. The selectivity to vinylnaphthalene decreased rapidly with conversion while the selectivity to ethylnaphthalene increased rapidly. This behavior is consistent with vinylnaphthalene undergoing secondary reaction to produce ethylnaphthalene. The rapid conversion of styrene to ethylbenzene has been observed by previous investigators (Klein and Virk, 1983; Savage and Klein, 1987a), and we expect this conversion to be even faster for polycyclic vinylarenes (Church and Gleicher, 1976).

Figure 7c displays the selectivities to naphthalene and undecane as a function of UDN conversion. The *y*-intercepts for these two products were approximately zero, suggesting that naphthalene and undecane are products of rank greater than one: that is, they are not formed during the initial stages of the reaction. Note, however, that this does not necessarily require these to be secondary products. Indeed, the product pair, naphthalene and undecane, can be formed only via the cleavage of the aryl-alkyl C-C bond in UDN. Thus, these are

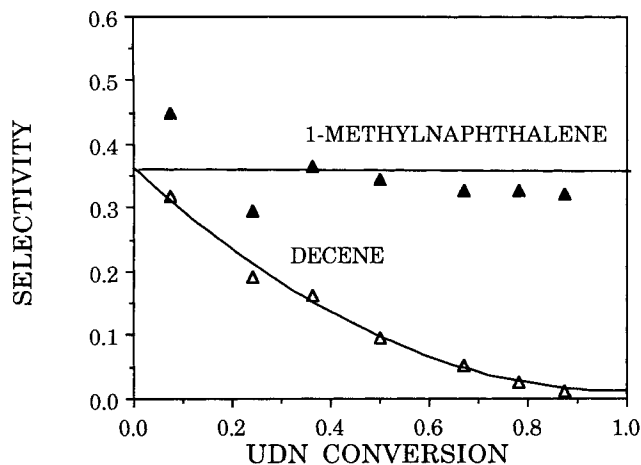


Figure 7a. UDN selectivity to major products (1-methylnaphthalene and decene).

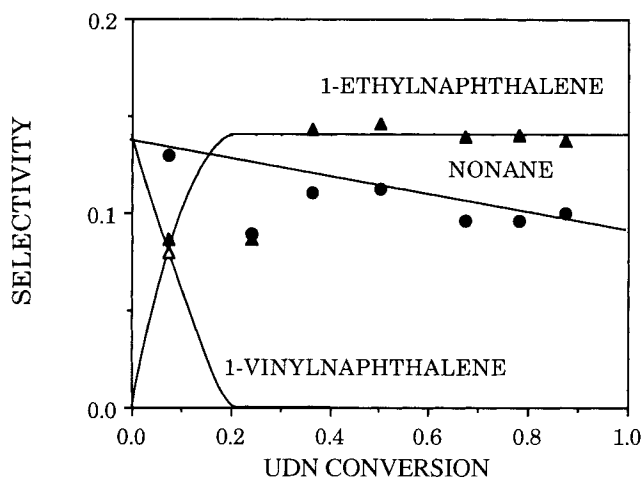


Figure 7b. UDN selectivity to major products (1-vinylnaphthalene, 1-ethylnaphthalene and nonane).

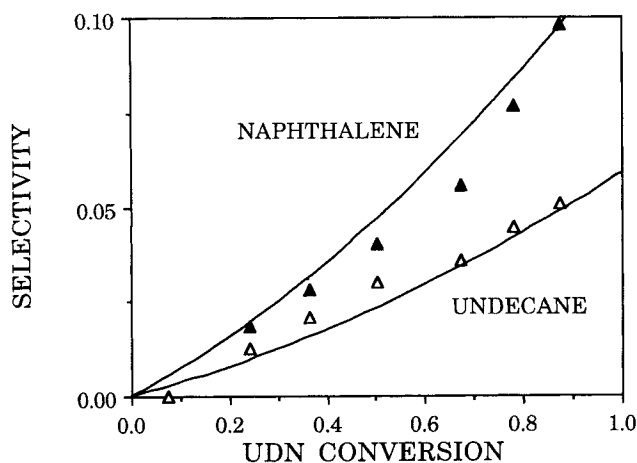


Figure 7c. UDN selectivity to major products (naphthalene and undecane).

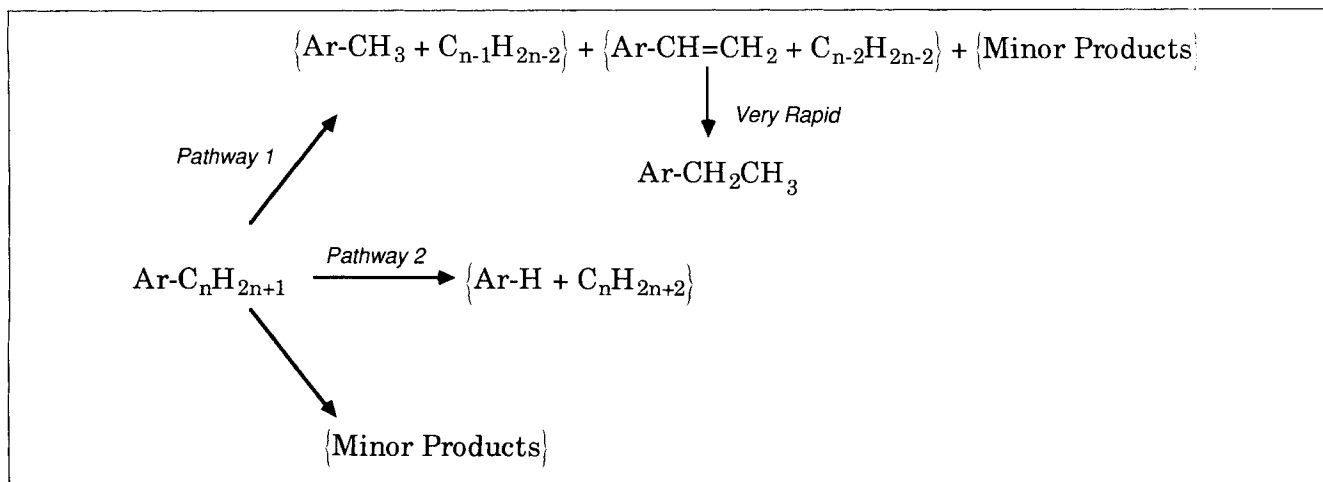


Figure 8. General pyrolysis network for alkyl-substituted aromatic hydrocarbons.

strictly primary reaction products. The zero initial selectivity and the steady increase in selectivity with UDN conversion are indicative of the formation of naphthalene and undecane through a primary autocatalytic pathway rather than through a secondary pathway.

We conducted similar reaction pathway analyses using the pyrolysis data for the other compounds, and the resulting pathways were completely analogous to those obtained from UDN pyrolysis. Therefore, the foregoing analysis has provided a general reaction network for the pyrolysis of alkylarenes. This pyrolysis network, shown in Figure 8, comprises three parallel primary pathways. The first pathway leads to the methylarene plus the C_{n-1} alkene as one product pair (for example, 1-methylnaphthalene and 1-decene for the UDN pyrolysis), the vinylarene and the C_{n-2} alkane as a second product pair (for example, 1-vinylnaphthalene and nonane for the UDN pyrolysis), and series of α -olefins, alkanes, alkylaromatics, and alkenylaromatics as a third grouping involving minor products. The second primary pathway for alkylarene pyrolysis leads to the arene and the C_n alkane (for example, naphthalene and n -undecane for the UDN pyrolysis). These products arise from the cleavage of the aryl-alkyl C-C bond. The final pathway allows for the formation of additional minor products such as those arising from condensation and cyclization reactions. This accounts for the visible amounts of char observed from several of the pyrolysis experiments. In addition to displaying the three parallel primary reactions, Figure 8 also displays the secondary conversion of vinylarene to ethylarene, among other products. This reaction is very rapid. Other secondary reactions also occur (for example, decomposition of alkenes, dealkylation of methyl-, vinyl- and ethylaromatics), but these are not shown explicitly in Figure 8.

Although the pathways in Figure 8 summarize the qualitative features of the pyrolysis of all of the alkylarenes studied, the quantitative features (such as selectivities) differed for the different compounds. For instance, the initial selectivities to methylarene at 400°C were 0.33 for UDN, 0.19 for BN, 0.22 for DDH, 0.0 for DDA, 0.2 for OC, and 0.0 for HP. The initial methylarene selectivities for pentadecylbenzene (Savage and Klein, 1987), DDB (Savage and Klein, 1987), and DDP (Savage et al., 1989a) were 0.35, 0.30, and 0.12, respectively. Further evidence that the relative importance of pathways 1

and 2 were compound-dependent is displayed in Figure 9. This figure provides the ratio of arene to methylarene selectivities as a function of alkylarene conversion for pyrolyses at 400°C. The ratios of arene to methylarene for DDB, DDH, UDN, and BN were all relatively low, indicating that pathway 1 was dominant for these compounds. The ratios of pyrene to methylpyrene and chrysene to methylchrysene were markedly higher; however, this indicates that the second pathway was also operative during the pyrolysis of DDP and OC. Finally, the ratios from DDA and HP pyrolyses, which are not shown in Figure 9, were extremely high because very low yields of methylarene were detected from these compounds. For DDA the ratio was always greater than 200, and for HP it was likewise large. A quantitative estimate, however, could not be determined for HP, because methylperylene was never present in yields sufficiently high to quantify. These high ratios indicate that pyrolysis proceeded nearly exclusively through the second pathway for DDA and HP. Thus, the qualitative features of the reaction network were the same for all of the compounds, but the relative importance of the different pathways varied depending on the specific compound being studied.

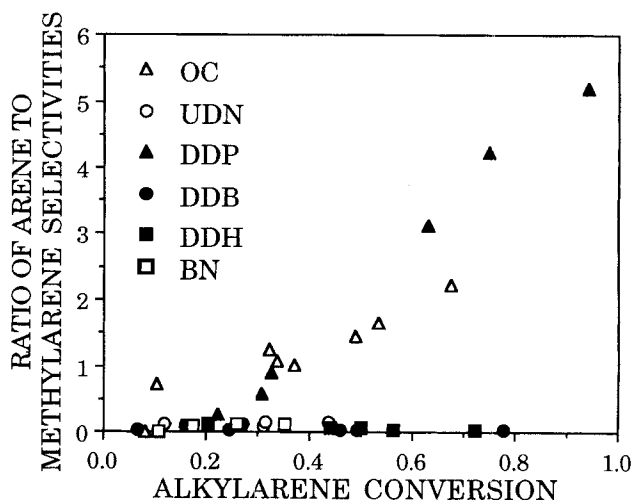


Figure 9. Effect of aromatic nucleus upon the relative selectivity of arene to methylarene.

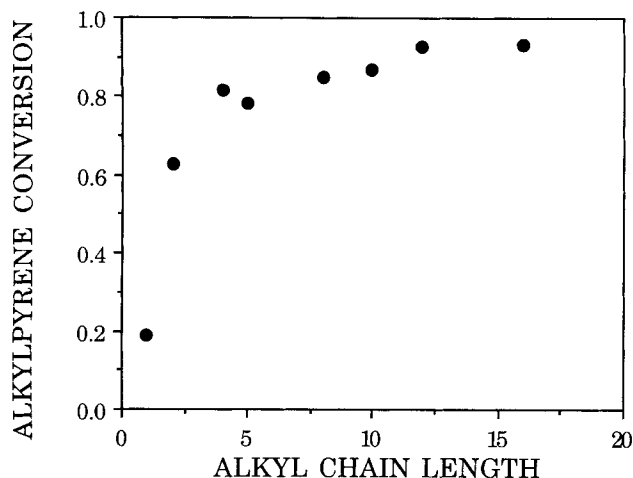


Figure 10a. Effect of alkyl chain length upon conversion for alkylpyrene pyrolysis at 400°C and 120 min.

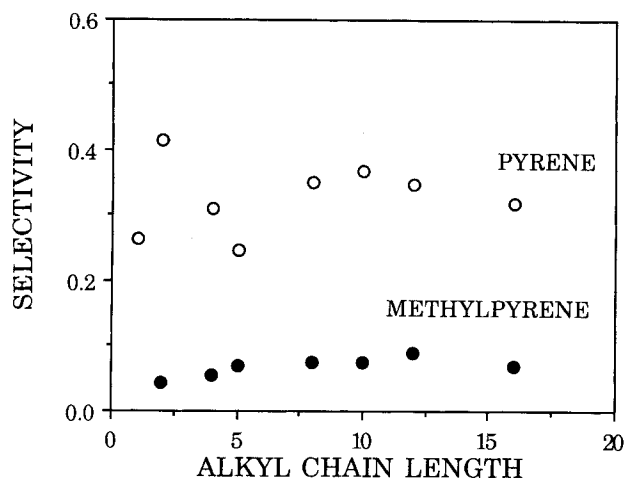


Figure 10b. Effect of alkyl chain length upon pyrene and methylpyrene selectivities for alkylpyrene pyrolysis at 400°C and 120 min.

In summary, our experimental results are consistent with the pyrolysis network shown in Figure 8, and with the identity of the aromatic moiety and the position of the substituent being key variables in determining the relative importance of pathways 1 and 2. Pathway 1 was the most important in guiding the pyrolyses of DDB, BN, DDH and UDN. Both pathways 1 and 2 were important for OC and DDP, but pathway 2 was the dominant route for the pyrolyses of DDA and HP.

Structure and reactivity

The previous section showed that the relative importance of pathways 1 and 2 depended on the structure of the *n*-alkylaromatic. This finding indicates that the structure of the compound influenced its reactivity. The two features that could be responsible for this structure-dependent reactivity are either the alkyl chain or the aromatic moiety.

To assess the influence of different alkyl chain lengths on the pyrolysis pathways and kinetics, we pyrolyzed a series of *n*-alkylpyrenes with aliphatic chains containing 1, 2, 4, 5, 8, 10, 12 and 16 carbon atoms. The neat pyrolyses were accom-

plished at 400°C for a batch holding time of 120 minutes. The reactant conversion for each of the alkylpyrenes in Figure 10a shows that the compounds with the longer chain lengths are more reactive. This result is consistent with previous results obtained from alkylbenzenes (Savage and Korotney, 1990). Note, however, that the variation in conversion with chain length is very small for long-chain (> C₄) *n*-alkylpyrenes, indicating that the chain length plays only a minor role in determining the overall reactivity.

Figure 10b provides the selectivities to methylpyrene and to pyrene as a function of the number of carbon atoms in the alkyl chain. We selected these two products because they are formed in pathways 1 and 2, respectively. The results in Figure 10b clearly show that the selectivities to the two different products were largely insensitive to the length of the alkyl chain. The selectivity to pyrene was always about 0.35, and the selectivity to methylpyrene was always around 0.07. Thus, the length of the alkyl chain does not have a strong influence on the relative importance of pathways 1 and 2.

The foregoing results lead us to conclude that the differences in reactivity and selectivity observed in the neat pyrolyses of the different alkylaromatics cannot be attributed to the different alkyl chain lengths these compounds possessed. Rather, the aromatic portion of the molecule must be the key to determining the reactivity and selectivity.

The effect of the structure of the aromatic portion of the reactants on their reactivity is discussed focusing on pathway 2, which involves cleavage of the aryl-alkyl C-C bond. The mechanism responsible for this pathway involves a hydrogenolysis reaction in which the alkyl substituent is displaced by hydrogen (Smith and Savage, 1991a,b), but the mechanistic details remain unresolved. Possible mechanisms include hydrogen atom *ipso*-substitution (Vernon, 1980), molecular disproportionation (Billmers et al., 1986, 1989), and radical hydrogen transfer (Malhotra and McMillen, 1990; McMillen et al., 1987). All of these mechanisms involve the transfer of a hydrogen atom from a donor to the *ipso*-position of the alkylaromatic thereby engendering aryl-alkyl bond cleavage. Thus, in essence, pathway 2 involves a substitution reaction in which the alkyl chain is replaced by a hydrogen atom.

For a family of aromatic substitution reactions, the change in energy of reaction can be attributed to that of the delocalized electrons (π -energy of the system, ΔE_π), provided that there is little or no change in energy of the localized bonds and in solvation (Dewar and Dougherty, 1975; Dewar 1969; Streitwieser, 1961). ΔE_π is a measure of the difference in the π -electron energy of the reactant aromatic system and the π -electron energy of the "Wheland intermediate" or σ -complex, and it is often termed the localization energy (Streitwieser, 1961). Invoking the Evans-Polanyi relationship (Boudart, 1968; Dewar and Dougherty, 1975; Dewar, 1969) then allows us to relate the change in activation energy, ΔE_a , between members of the reaction family with their corresponding change in ΔE_π . This result is given as Eq. 1 where α is the Evans-Polanyi factor:

$$\Delta E_a = \text{constant} + \alpha \Delta E_\pi \quad (1)$$

For even alternant hydrocarbons, ΔE_π can be calculated readily from perturbation molecular orbital theory (Dewar and Dougherty, 1975; Dewar 1969; Streitwieser, 1961) as:

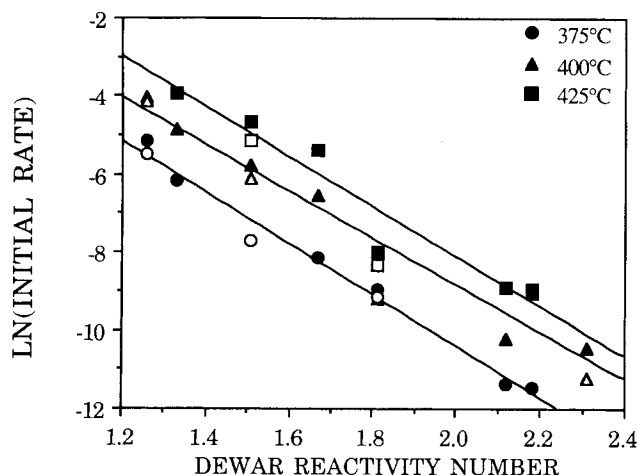


Figure 11. Correlation of initial rate of aryl-alkyl bond cleavage in alkylarene pyrolysis with the Dewar reactivity numbers.

$$\Delta E_{\pi} = 2\beta(a_{or} + a_{os}) = \beta N_t \quad (2)$$

where β is the resonance integral, and a_{or} and a_{os} are the coefficients of the nonbonding molecular orbitals at the positions adjacent to the position of substitution, which is denoted by the subscript t . The quantity $2(a_{or} + a_{os})$ is defined as the Dewar reactivity number N_t . Dewar (1952) and Gore (1954) provide values of this reactivity number for a large number of different compounds, and the values relevant to the present study were given in Figure 1 and Table 7.

Combining Eqs. 1 and 2 shows that:

$$\Delta E_a = \text{constant} + \alpha\beta N_t \quad (3)$$

Equation 3 suggests that a semilog plot of the reaction rate constants for aromatic substitution reactions as a function of the Dewar reactivity number N_t should be linear. The literature presents many such correlations of reactivity in aromatic substitution reactions with a measure of the localization energy (Altshuler and Berliner, 1966; Dickerman et al., 1973; Dewar and Thompson, 1965).

To develop a correlation using the present results, we calculated the initial rate of aryl-alkyl bond cleavage for each of the alkylaromatics studied. Ideally, it would be desirable to correlate a reaction rate constant with the Dewar reactivity number. Calculating the value of the rate constant, however, requires a knowledge of the hydrogenolysis rate law, which unfortunately is unknown. Thus, we chose to employ initial rates. These rates were calculated as the initial slope of the molar yield vs. time curve for both the arene and, when possible, for the corresponding n -alkane. Figure 11 displays the natural logarithm of the initial rate of aryl-alkyl bond cleavage as a function of the Dewar reactivity number of the alkylarenes used in this study and for compounds pyrolyzed previously (Savage et al., 1989; Savage and Klein, 1987b). The open symbols represent those rates calculated from the alkane, and the filled symbols represent rates calculated from the arene. The correlation of the initial rates with the Dewar reactivity number is clearly linear for all three temperatures.

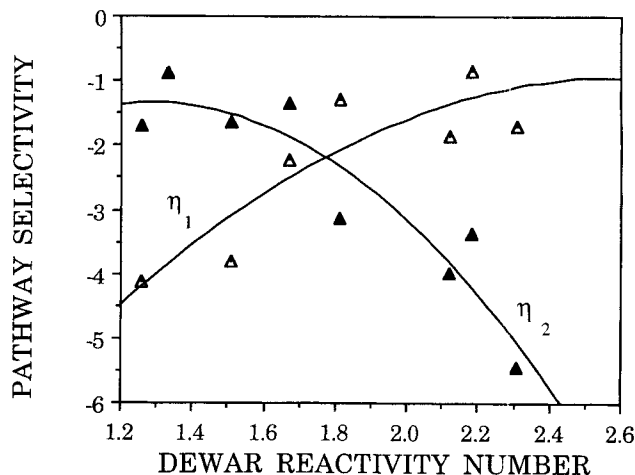


Figure 12. Correlation of pathway selectivity with Dewar reactivity number for alkylarene pyrolysis at 400°C.

The slopes of the lines in Figure 11 are equal to $\alpha\beta/RT$ where R is the gas constant and T is the pyrolysis temperature. The quantity $\alpha\beta$, sometimes termed β_x , was calculated to be 8.6 ± 1.2 kcal/mol at the 95% confidence interval. This quantity provides insight into the mechanism of the substitution reaction and the relative position of the transition state along the reaction coordinate because it is a measure of how closely the transition state resembles the σ -complex. High values of β_x imply late transition states and selective reactions whereas low values of β_x imply early transition states and less selective substitution reactions.

To place the present value of $\beta_x = 8.6$ kcal/mol within the context of other work with aromatic substitution reactions, we note that $\beta_x = 3.4$ for phenylation, 4.7 for nitration, 5.5 for methylation, 7.5 for deuteriodeprotonation, 14.5 for chlorination, and 16.1 for bromination (Altshuler and Berliner, 1966; Dickerman et al., 1973). Thus, bromination has the latest transition state, and phenylation has the earliest transition state. The magnitude of β_x obtained from our analysis indicates that the transition state occupies an intermediate position along the reaction coordinate between the highly selective chlorination reaction and the less selective deuteriodeprotonation reaction. Therefore, we conclude that the mechanism responsible for engendering the aryl-alkyl C-C bond cleavage is moderately selective. This conclusion is consistent with our previous experimental results (Smith and Savage, 1991a,b).

Figure 11 is useful, not only because it summarizes a large set of experimental kinetics data and provides some mechanistic insight, but also because it possesses predictive capabilities: that is, the initial rate and relative importance of aryl-alkyl cleavage for any n -alkylaromatic can be predicted *a priori* from Figure 11. For instance, a 1-alkylanthracene, which has a Dewar number of 1.57, is expected to undergo facile aryl-alkyl cleavage, whereas a 2-alkyltriphenylene, which has a much higher Dewar number of 2.12 will undergo very little aryl-alkyl cleavage. Its pyrolysis will follow pathway 1 predominantly. To summarize, we have successfully correlated the rate of aryl-alkyl bond cleavage for the pyrolysis of alkyl-substituted aromatic compounds with the structure of the aromatic moiety using results from perturbation molecular orbital theory.

As one additional correlation of structure and reactivity, consider Figure 12. Here we use semilog coordinates to plot the selectivities toward pathways 1 and 2 vs. the Dewar reactivity number. The selectivity toward pathway 1, η_1 , was calculated as the ratio of the initial rate of methylaromatic formation to the pseudo-first-order rate constant for alkylarene disappearance. Likewise, the selectivity toward pathway 2, η_2 , was calculated as the ratio of the initial rate of arene formation to the pseudo-first-order rate constant for alkylarene disappearance. The results show that η_2 is high and essentially Dewar-number invariant for compounds with low Dewar numbers (e.g., <1.6). As the Dewar number increases, however, η_2 decreases in a nearly linear fashion. Conversely, η_1 increases as the Dewar number increases, and this behavior indicates an increase in the importance of pathway 1. Thus, as the Dewar number changes in Figure 12, the relative importance of the two pathways shifts. These results are entirely consistent with our previous assertion that *n*-alkylarenes fall into one of three categories. Compounds with low Dewar numbers pyrolyze predominantly via pathway 2. Compounds with high Dewar numbers pyrolyze predominantly via pathway 1. Compounds with intermediate Dewar numbers experience contributions from both pathways 1 and 2.

The data in Figure 12 are also consistent with the pseudo-first-order rate constants in Table 7 exhibiting a minimum at an intermediate Dewar number. This type of behavior emerges because the pyrolysis of *n*-alkylarenes involves two major parallel primary pyrolysis pathways with different dependencies on the Dewar number. Briefly, at high Dewar numbers pathway 1 predominates, and the rate of this pathway decreases as the Dewar number decreases. Thus, the pseudo-first-order rate constant initially decreases. As the Dewar number continues to decrease, however, the rate of pathway 2 becomes more significant, and the reaction via this new pathway more than compensates for the loss in reactivity in pathway 1. Thus, the pseudo-first-order rate constant reaches a minimum value and then increases with further decreases in the Dewar number.

Finally, it is interesting to note that the shape of the curve for η_2 is reminiscent of that for the effectiveness factor as a function of the Thiele modulus. Such a curve arises in heterogeneous catalysis for largely the same types of reasons. There are two rate processes (diffusion and reaction), and the relative importance of the processes shifts with the value of the Thiele modulus.

Conclusions

- The pyrolysis of alkyl-substituted polycyclic aromatic compounds proceeds through three parallel pathways. The first of the two major pathways leads to three product lumps that are analogous to those observed for alkylbenzene pyrolysis. The second major pathway leads to products through the cleavage of the strong aryl-alkyl C-C bond. The third pathway, which is a minor one, leads to hydrogen-deficient products.

- The importance of aryl-alkyl C-C bond cleavage during the pyrolysis of polycyclic alkylaromatics depends primarily on the localization energy at the specific point of substitution. The occurrence of aryl-alkyl C-C bond cleavage was independent of the number of rings, the length of the alkyl chain, and the type of condensation of the aromatic nucleus.

- A quantitative correlation exists between the Dewar reactivity number, which can be easily calculated from perturbation

molecular orbital theory, and the rate of aryl-alkyl C-C bond cleavage during the pyrolysis of *n*-alkylarenes. This correlation provides a link between the structure and the reactivity of polycyclic *n*-alkylaromatics and suggests that the mechanism responsible for the aryl-alkyl C-C bond cleavage is moderately selective.

- The differences in the relative importance of pathways 1 and 2 for the pyrolysis of the *n*-alkylarenes used in this study suggest that three different categories exist for these compounds. Pathway 1 is dominant for compounds in the first category, and these compounds had Dewar reactivity numbers greater than 1.81. Both pathways 1 and 2 are important for compounds in the second category, and these compounds had Dewar reactivity numbers between 1.51 and 1.67. Pathway 2 is dominant for compounds in the third category, and these compounds had Dewar reactivity numbers less than 1.33.

Acknowledgment

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