

PYROLYSIS OF COMPOUNDS CONTAINING POLYCYCLIC AROMATIC MOIETIES

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INTRODUCTION

Coal is thought to exist in a complex, cross-linked, macromolecular framework in which polycyclic moieties are covalently linked together by aliphatic and heteroatomic bridges (1-3). The condensed aromatic groups can also bear peripheral, non-bridging moieties, including long aliphatic chains (4).

The pyrolysis of numerous compounds mimicking these structural features has provided considerable insight to the thermal reactions of coal. Previous pyrolyses were typically of compounds containing a single aromatic ring, which was intended to mimic the more massive condensed aromatic moieties in coal. It is possible, however, that single-ring compounds might not display the same reaction pathways and kinetics as otherwise identical compounds containing polycyclic aromatic moieties.

One difference between a single aromatic ring and the condensed aromatic moieties in coal is their sizes. This difference suggests that the model-compound-derived free radicals could be considerably more mobile than their coal-derived counterparts. To probe the influence of radical mobility on pyrolysis pathways Poutsma and coworkers (5-7) pyrolyzed coal model compounds immobilized on silica surfaces. They found that surface immobilization can lead to an enhancement of unimolecular pathways relative to bimolecular ones.

In an attempt to gain additional insight into the fundamentals of coal pyrolysis, and particularly the effects of condensed aromatics, we recently initiated experiments with compounds containing polycyclic aromatic moieties, which better represent the aromatic clusters in coal than do single-ring compounds. In this paper, we report on the pyrolysis of two compounds; 2-(3-phenylpropyl)-naphthalene (PPN), and 1-dodecylpyrene (DDP).

EXPERIMENTAL

PPN and DDP were pyrolyzed at isothermal temperatures between 350 and 425°C for batch holding times between 10 and 180 min.

Materials.

All chemicals were obtained commercially; 1-Dodecylpyrene (DDP) from Molecular Probes and 2-(3-phenylpropyl)-naphthalene (PPN) from API Standard Reference Materials, and used as received. The nominal purity of each compound was > 99%, and this was confirmed by GC analysis. PPN pyrolyses were accomplished in 1.5 x 100 mm Kimax glass capillary tubes, and DDP pyrolyses were in nominal 3/8" tubing bomb microreactors. The latter reactors were fashioned from a single Swagelok stainless steel port connector and two caps. The glass reactors were not routinely used with DDP because it is a fluffy solid and was difficult to load into the small diameter tubes. However, one experiment was done in a glass reactor to verify the absence of catalysis by the stainless steel surfaces in the tubing bomb microreactor.

Procedure.

The tubing bomb microreactors were typically loaded with about 10 - 30 mg of DDP and then about 10 mg of biphenyl was added to serve as an internal standard in the chromatographic analyses. All quantities were carefully (± 0.1 mg) weighed. The glass capillary tubes used for PPN pyrolyses were typically charged with 10 μ l of a previously prepared stock solution containing the model compound and the internal standard. The reactors were then sealed and immersed in a preheated, fluidized sand bath. After the desired reaction time had elapsed, the reactors were removed from the sand bath, rapidly cooled to room temperature to quench the reaction, and then opened. Reaction products were extracted in spectrophotometric grade acetone and analyzed by GC and GC-MS. Molar yields were calculated as the number of moles of product divided by the number of moles of reactant initially charged to the reactor.

RESULTS

The experimental results are presented primarily as the temporal variations of the products' molar yields. Tables I and II provide representative results for PPN and DDP, respectively, at each of the temperatures investigated. Based on the reproducibility of the results we estimate the uncertainty in product molar yields for PPN and DDP to be roughly $\pm 10\%$ and $\pm 25\%$, respectively.

PPN Pyrolysis.

PPN pyrolysis at 350°C yielded toluene, styrene, 2-methylnaphthalene, and 2-vinylnaphthalene as the major products, and at 60 min traces of ethylbenzene and 2-ethylnaphthalene were also detected. GC-MS analysis of the reaction products permitted tentative identification of two additional minor products as 2-isopropylnaphthalene and 1,3-diphenylpropane. The pseudo-first-order rate constant for PPN disappearance was 0.007 min^{-1} .

Figure 1, which displays the temporal variation of the major products from PPN pyrolysis at 375°C, shows that the yields of toluene and 2-methylnaphthalene increased steadily throughout the 60 min reaction. The yields of styrene and 2-vinylnaphthalene decreased with holding time. The yields of ethylbenzene and 2-ethylnaphthalene were zero at short times, but they reached 6.2% and 8.5%, respectively at 60 minutes. The pseudo-first-order rate constant for PPN conversion at 375°C was 0.028 min^{-1} .

PPN pyrolysis at 400°C proceeded rapidly and was essentially complete at 60 min. Toluene and 2-methylnaphthalene were the major products, but the yields of ethylbenzene and 2-ethylnaphthalene were also substantial. The product alignment at 60 min was toluene (52%), 2-methylnaphthalene (48%), 2-ethylnaphthalene (19%), ethylbenzene (19%), styrene (0.8%), and 2-vinylnaphthalene ($< 0.1\%$). The pseudo-first-order rate constant was 0.076 min^{-1} .

Figure 2 presents the variation of the major products' molar yields with PPN conversion. Toluene and 2-vinylnaphthalene were present in nearly equal yields at low conversions. The yield of toluene increased to roughly 50% at complete conversion, whereas the yield of 2-vinylnaphthalene went through a maximum value (3.6%) and then decreased to 0. The yield of 2-ethylnaphthalene was very low at conversions $< 30\%$, but it increased rapidly at very high conversions. The yield of 2-methylnaphthalene increased steadily with conversion to an ultimate value of nearly 50%. The yield of styrene, like that of 2-vinylnaphthalene, exhibited a maximum value and then decreased to zero. Finally, the yield of ethylbenzene was very low for conversions less than 50%, but it increased to 19% when conversion was nearly complete.

The disappearance of PPN correlated well with first-order kinetics, and the Arrhenius parameters for the pseudo-first-order rate constant were $[\log_{10} A (\text{sec}^{-1}), E^* (\text{kcal/mol})] = [10.0, 39.8]$.

DDP Pyrolysis.

DDP pyrolyses led to pyrene, methylpyrene, dodecane, nonane, and undecene as the major products at short reaction times. Minor products included series of n-alkanes ($C_8 - C_{12}$), α -olefins ($C_8 - C_{12}$), and alkylpyrenes. GC-MS analysis revealed the presence of a compound tentatively identified as pyrenylpropene. No other pyrenylalkenes were present in yields sufficiently high to be quantified. In addition to the molecular products noted above, an acetone-insoluble char formed as a result of DDP pyrolysis.

The yields of each of the major products from DDP pyrolysis at 375°C increased with batch holding time. The ultimate yields of pyrene, dodecane, nonane, methylpyrene, and undecene were 52%, 28%, 7.0%, 6.7%, and 1.4%, respectively, at 180 min. The yields of several n-alkanes and ethylpyrene increased more rapidly than did the yield of undecene, and these products were more abundant than undecene at the more severe conditions.

The major products from DDP pyrolysis at 400°C and at short times were pyrene, dodecane, methylpyrene, nonane, and undecene. At longer batch holding times the yields of some n-alkanes increased and surpassed the undecene yield, which reached a maximum value of 1.9% at 60 min. The yields of pyrene, dodecane, nonane, and methylpyrene increased with time and achieved ultimate values of 49%, 32%, 9.4%, and 8.3%, respectively at 180 min.

DDP pyrolysis at 425°C was rapid and essentially complete at 45 min. The major products at short reaction times were the same as those observed at the lower temperatures, and Figure 3 displays the temporal variation of their yields. The yields of pyrene, dodecane, nonane, and methylpyrene were relatively time invariant after 60 minutes, and their ultimate values were approximately 49%, 25%, 10%, and 10%, respectively. Undecene, on the other hand, exhibited a maximum yield of 3.1% at 15 min and then its yield decreased to undetectable levels at 120 min.

Figure 4 displays the distribution of alkanes and olefins produced from DDP pyrolysis at 425°C and 17 min. The alkane distribution exhibits a peak at nonane (C₉) and a higher one at dodecane (C₁₂). The olefinic products were relatively evenly distributed with the exception of the high undecene yield. Note that with the exception of C₁₁, alkanes were present in yields higher than the corresponding olefins.

DISCUSSION

PPN Pyrolysis.

Figure 2 shows that the product pairs toluene plus 2-vinylnaphthalene and 2-methylnaphthalene plus styrene were present in nearly equal yields at low conversions. This is consistent with the formation of each product pair in a common reaction step. Furthermore, the non-zero initial slopes apparent in the molar yield vs. time curves (i.e., Figure 1) for each of these four products indicates that these are primary reaction products. On the other hand, the initial slopes associated with 2-ethylnaphthalene and ethylbenzene are zero, thus these are secondary products. That the yields of 2-vinylnaphthalene and styrene go through a maximum and then decrease to zero is consistent with their participating in secondary reactions. Toluene and 2-methylnaphthalene were apparently stable at the temperatures studied.

These observations combine to suggest the reaction pathway shown in Figure 5 for PPN pyrolysis. The nearly equal yields of 2-methylnaphthalene and toluene (e.g., both were nearly 50% at essentially complete PPN conversion) indicate that the stoichiometric coefficients ν_1 and ν_2 are both approximately equal to 0.5.

The primary pyrolysis pathway deduced for PPN is essentially the same as that reported for 1,3-diphenylpropane (8-10), the single-ring analogue of PPN. This suggests that, in this instance, substituting a naphthyl for a phenyl moiety does not detectably alter the operative reaction pathways or the reaction mechanism. Note however that this is not true of the reaction rates. The pseudo-first-order rate constants for PPN reported here were 4-10 times as high as pseudo-first-order rate constants determined from data presented by Poutsma and Dyer (8) for the liquid-phase pyrolysis of diphenylpropane. [Note: diphenylpropane pyrolysis was reported to be 3/2 order (8,9) thus the calculated pseudo-first-order rate constants are the product of the intrinsic rate constant and the square root of the concentration. We used the highest reaction rates reported (e.g., for liquid-phase pyrolyses) to calculate pseudo-first-order rate constants for diphenylpropane.]

DDP Pyrolysis.

Some aspects of DDP pyrolysis are consistent with previous results from the thermal cracking of dodecylbenzene (11,12) and other long-chain n-alkylbenzenes (13,14). Dodecylbenzene pyrolysis (11, 12) was via a free-radical mechanism, and the two pairs of major products, toluene plus undecene and styrene plus decane, arose from β -scission of a γ and an α -dodecylbenzene radical, respectively. The minor products comprised complete series of n-alkanes, α -olefins, alkylbenzenes, and phenylalkenes. Only traces of benzene were detected.

Elements of similar free-radical reactions appear to be operative in DDP pyrolysis. Methylpyrene and undecene were present in relatively high yields at mild reaction conditions, and these are the expected ultimate products from β -scission of a γ -DDP radical. Similarly the product pair nonane plus pyrenylpropene could have been formed via β -scission of a β -DDP radical. Finally, as observed in dodecylbenzene pyrolysis, series of alkanes and olefins and some alkylaromatics were produced as minor products from DDP pyrolysis.

Although some aspects of DDP pyrolysis parallel those of its single-ring analogue, there are several interesting differences. The appearance of pyrene and dodecane as the major products from DDP pyrolysis indicates that rupture of the aryl-alkyl C-C bond was facile. This is not expected on the basis of the free-radical reaction mechanism proposed (12) for dodecylbenzene because this C-C bond is the strongest in the

alkyl chain and hence most resistant to cleavage. Furthermore, the alkane distribution for DDP pyrolysis showed a peak at n-nonane, but no such preferential formation of nonane was observed in the pyrolysis of n-alkylbenzenes (11-14).

Finally, pyrene and dodecane together contain more hydrogen than the reactant, DDP. Thus formation of these as major products requires the simultaneous formation of hydrogen-deficient products in relatively high yields. GC analyses revealed no such products, thus we conclude that the experimentally observed, acetone-insoluble char was the source of this hydrogen.

SUMMARY AND CONCLUSIONS

The pyrolytic pathway for PPN was identical to that of its single-ring analogue, 1,3-diphenylpropane. The apparent first-order kinetics of PPN disappearance were 4-10 times more rapid however. On the other hand, both the pathways and kinetics of DDP pyrolysis differed from those of its single-ring analogue, dodecylbenzene. The major products of DDP pyrolysis, pyrene and dodecane, indicate that bond cleavage occurred predominantly at the ring, whereas the primary pathways in dodecylbenzene pyrolysis involved cleavage of the covalent bonds between the α and β carbons and the β and γ carbons to produce toluene plus undecene and styrene plus decane, respectively. The results of this study demonstrate that the thermal reaction pathways and kinetics of compounds containing condensed aromatic moieties can differ from those of their single-ring analogues.

ACKNOWLEDGEMENT

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TABLE I: Yields (%) of Major Products from PPN Pyrolysis

TIME (min) →	350°C			375°C			400°C		
	10	31	61	11	30	60	20	30	60
Toluene	2.0	5.7	10.	7.8	20.	35.	39.	44.	52.
Ethylbenzene	-	-	0.6	-	1.5	6.2	6.9	11.	19.
Styrene	1.9	3.5	3.8	10.	6.0	4.1	7.1	4.5	0.8
2-Methylnaphthalene	2.2	6.2	11.	8.2	21.	35.	39.	43.	48.
2-Ethyl-naphthalene	-	-	1.0	-	2.4	8.5	9.7	14.	19.
2-Vinylnaphthalene	1.8	2.1	2.1	3.5	2.9	1.5	2.8	1.2	-
PPN	88.	78.	64.	77.	44.	20.	15.	8.4	1.1

TABLE II: Yields (%) of Major Products from DDP Pyrolysis

TIME (min) →	375°C			400°C			425°C		
	60	120	180	30	90	180	11	60	120
Hexene	-	-	-	-	-	-	-	1.3	1.5
Hexane	-	-	-	-	1.5	2.6	-	4.1	8.5
Heptene	-	-	-	-	-	-	-	1.1	1.5
Heptane	-	-	1.1	-	1.3	2.2	-	3.2	5.6
Octene	-	-	-	-	-	-	-	0.9	0.8
Octane	0.4	1.2	1.7	0.5	2.0	3.2	-	4.0	5.9
Nonene	-	-	-	-	-	-	-	0.7	0.6
Nonane	1.4	4.9	7.0	2.8	7.7	9.4	2.6	10.	13.
Decene	-	-	-	-	-	-	-	0.6	0.6
Decane	0.7	1.6	2.3	1.5	3.6	4.5	2.0	5.5	6.9
Undecene	0.8	1.2	1.4	1.8	1.2	-	2.5	1.1	-
Undecane	0.5	2.0	3.5	0.8	4.9	6.5	-	6.4	7.7
Dodecene	-	-	0.6	-	0.6	-	-	0.9	-
Dodecane	4.5	19.	28.	9.6	28.	32.	6.9	25.	28.
Pyrene	8.6	46.	52.	17.	40.	49.	12.	48.	50.
Methylpyrene	2.0	6.3	6.7	3.6	5.5	8.3	4.4	10.	10.
Ethylpyrene	0.7	2.2	2.1	1.6	1.9	1.8	2.4	2.5	1.7
Pyrenylpropene	-	-	-	2.2	-	-	1.9	-	-
DDP	69.	68.	36.	46.	4.8	-	51.	-	-

Note: - indicates product yields too low to be determined quantitatively

FIGURE 1: TEMPORAL VARIATION OF PRODUCT YIELDS FROM PPN PYROLYSIS AT 375C

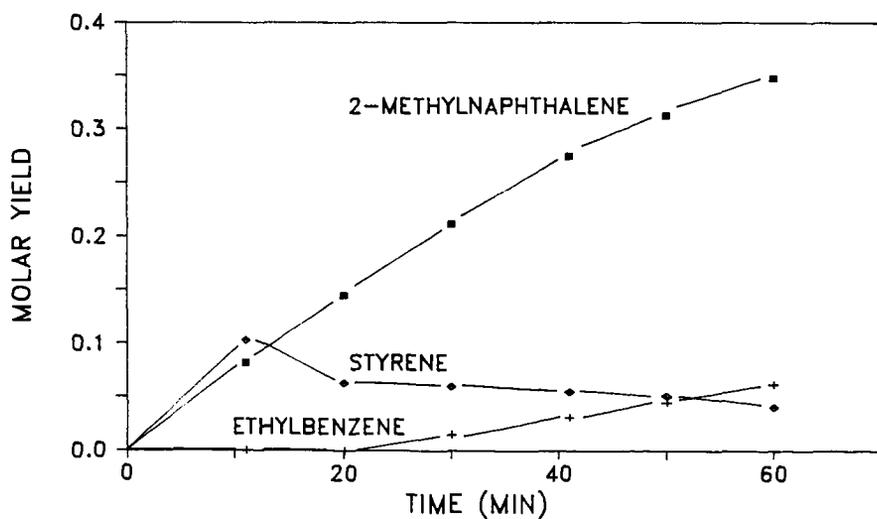
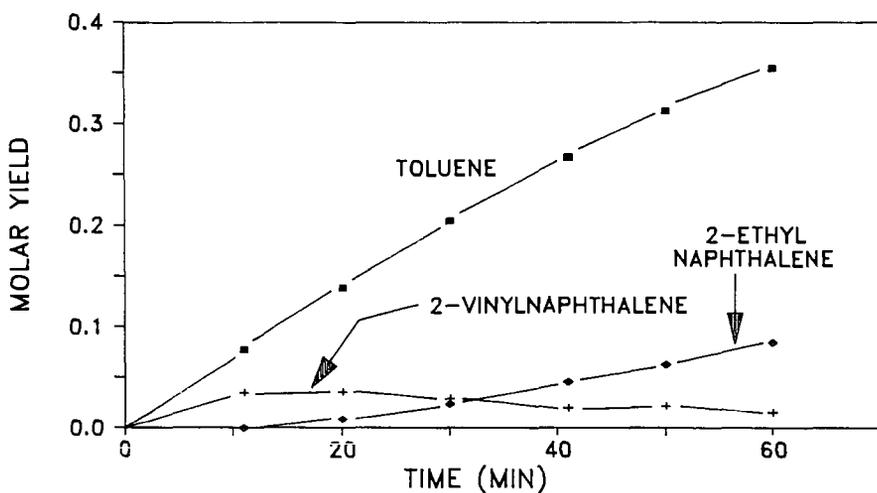


FIGURE 2: VARIATION OF PRODUCT YIELDS WITH PPN CONVERSION

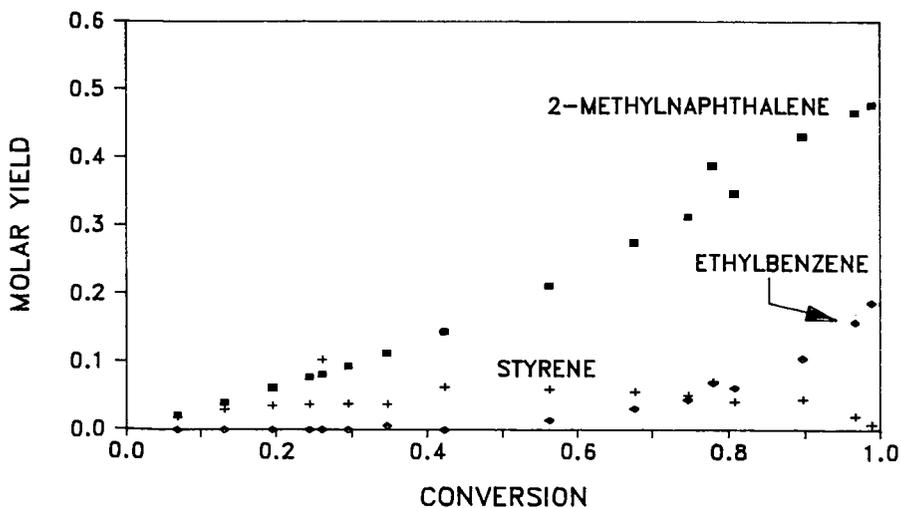
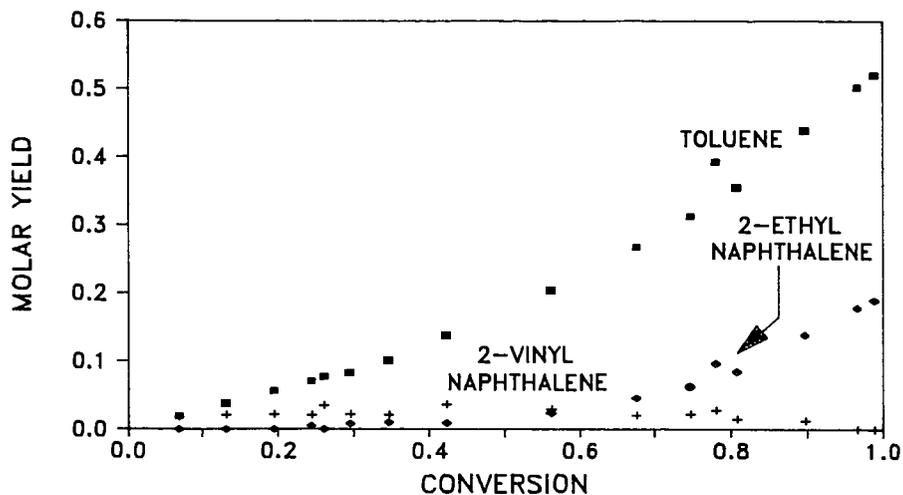


FIGURE 3: TEMPORAL VARIATION OF PRODUCT YIELDS FROM DDP PYROLYSIS AT 425C

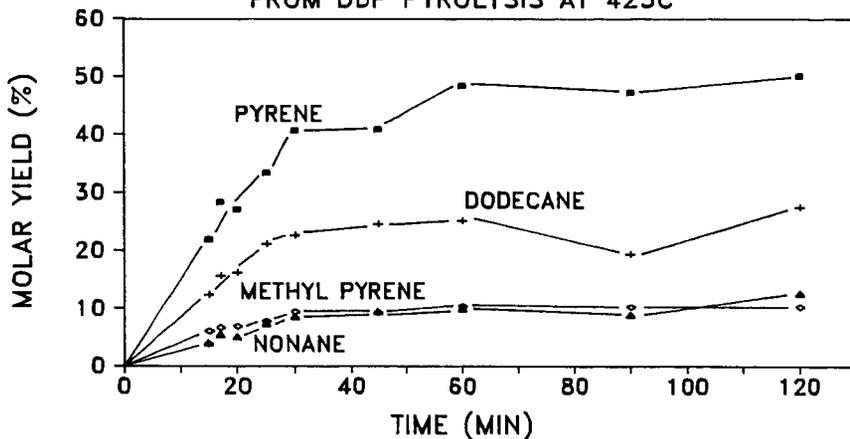


FIGURE 4: VARIATION OF OLEFIN AND ALKANE YIELDS FROM DDP PYROLYSIS (425C, 17 MIN)

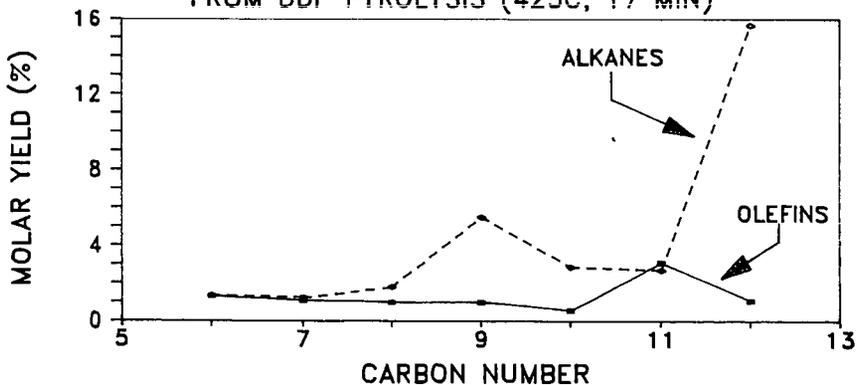


FIGURE 5: PPN PYROLYSIS PATHWAY

