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Pyrolytic Hydrocarbon Growth from Cyclopentadiene

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Aromatic hydrocarbon growth from cyclopentadiene (CPD) was studied using a laminar flow reactor operating in the temperature range 550−950 °C without oxygen. Benzene, indene, and naphthalene were the major products, which is in agreement with the previous computational studies on the reaction pathways from CPD. A crossover of indene and naphthalene yields around 775 °C was also observed, which further supports the results of the computational studies. Although the specific intermediates in the proposed pathways from CPD were not detected, the high selectivity of products and the observation of other methylindene and dihydronaphthalene intermediates suggest that the recombination of two CPDs via radical−molecule and/or radical−radical pathways to form indene and naphthalene is the dominant formation pathway. In addition to the products from the CPD−CPD reactions, the products from the reactions of CPD with indene, naphthalene, and acenaphthylene were also observed, which demonstrate the importance of CPD in carbon growth.

Introduction

The formation of five-membered rings in combustion is of particular interest due to the high reactivity[1,2] and toxicity of many compounds that contain these moieties.[3,4] Polycyclic aromatic hydrocarbons (PAHs) with peripherally fused five-membered rings demonstrate a greater facility to undergo certain kinds of reactions, such as dimerization and isomerization involving intramolecular rearrangement, than PAHs without these moieties.[1,2,5−7] Although the hydrogen-abstraction and acetylene-addition (HACA) mechanism has been shown to be an important mechanism of PAH formation in flames,[8−13] the HACA mechanism alone cannot explain the formation of many large PAHs in flames that are thermodynamically unfavorable or that are too slow kinetically.[14] Violi and co-workers[6,15,16] suggested that high molecular mass structures, soot inception, and particulate mass growth occur in oxidative environments predominantly through fast reactions of small PAH rather than acetylene.

Among many potenital precursors for aromatic growth, the cyclopentadienyl (CPDyl) radical is considered to be an important intermediate in PAH formation due to its multiple reaction sites and its ability of self-recombination,[17,18] which also resulted in increased formation of aromatic products.[19] The CPDyl radical contribution to PAH growth has been observed from naphthalene formation in flames.[14,20−22] In addition, computational studies[23,24] proposed a formation pathway to naphthalene from CPDyl radicals. A detailed chemical mechanism by Melius et al.[24] proposed dimerization of CPDyl radicals to form 9,10-dihydrofulvalene, followed by conversion of five-membered rings to six-membered rings. Ritcher et al.[25] suggested the self-recombination of CPDyl radicals to be the major pathway to naphthalene in benzene flames from their premixed flame experiment. Mulholland and co-workers[26−28] investigated experimentally and computationally detailed pathways to PAH growth from cyclopentadiene and indene in the postflame conditions. Butler and Glassman[29] also reported that indene and naphthalene were major products from CPD combustion in a plug flow reactor at 1150 K.

Recently, various pathways leading to naphthalene, indene, and benzene from the addition of the CPDyl radical to cyclopentadiene (CPD) were studied at the B3LYP/6-31G** level.[15] Proposed intermediates included 4- and 7-methylindenes and 9,10-dihydronaphthalene. Kislov and Mebel[30] reported ab initio Gaussian 3 (G3)-type calculations of reaction routes from CPD to naphthalene, azulene, and fulvalene. They suggested additional routes leading to naphthalene via the azulene−naphthalene isomerizartion. Later, Kislov and Mebel[31] also calculated the potential energy surface for possible rearrangements of reaction products of CPDyl radical recombination and the intermolecular addition of the CPDyl radical to CPD and proposed the detailed picture of reaction pathways from CPD to indene, naphthalene, azulene, and fulvalene.

Although the theoretical investigations provided more detailed information on both stable and radical species in the CPD reaction pathways, the CPD chemistry in a real combustion system is expected to be much more complicated. In addition to the radical−radical/radical−molecule reactions of two CPDs, reactions between CPD and other species in the system and other competitive pathways than those suggested are possible, which would result in different reaction products and their yields. Therefore, hypothesized CPD reaction routes need to be tested and refined on the basis of experimental work. In this paper, we present the observed aromatic hydrocarbon products from CPD using a laminar flow reactor. This experimental study complements the theoretical investigations of the CPD chemistry and provides a better understanding of the CPD chemistry in carbon growth.

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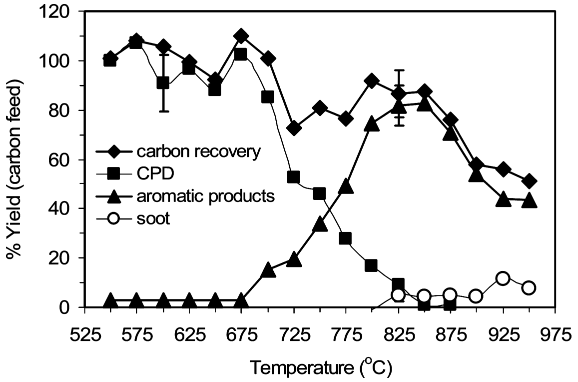


Figure 1. Overall reaction profile from CPD pyrolysis.

Experimental Methods

The laminar flow reactor system used for CPD pyrolysis consists of a Thermolyne Model 21100 furnace, a digital temperature controller, and a quartz tube of 48 cm long and 1.7 cm in diameter (Figure S1, Supporting Information).[26] Temperature profiles inside the quartz tube reactor were measured using a thermocouple for different temperature settings, and measurements of the reactor temperature profiles indicate that temperatures at the top 8 cm and bottom 9 cm of the quartz tube are lower than the set value (Figure S2, Supporting Information). The gas temperatures in the remaining 31 cm of the reactor, defined as a reaction zone, are approximately constant within ±10 °C of the set value. Radial variation of temperature was negligible.

Dicyclopentadiene (DCPD) with 99.9% purity (Chem Service, Inc., West Chester, PA, U.S.) was heated to liquid form (34 °C) and fed by a syringe pump into a glass vessel. The glass vessel was wrapped with a heat tape to ensure the temperature would be 20 °C above the boiling point of DCPD (180 °C); the temperature in the glass vessel was monitored by a thermocouple. At the outlet of the glass vessel, DCPD was more than 99.9% decomposed to CPD. Nitrogen was used as a carrier gas, and the gas stream entering the reactor consisted of 0.7% molar CPD vapor in nitrogen. Experiments were conducted at temperatures ranging from 550 to 950 °C; triplicate experiments were conducted at 825 °C, the temperature at which total aromatic product yield was greatest. A nominal residence time of 3 s was maintained; the mass flow rate was held constant so the actual residence time varied slightly with reactor temperature. The product stream was quenched at the outlet of the reactor and collected in a dual ice-cooled dichloromethane (DCM) trap.

After each experiment, the quartz tube, all fittings, and collection trap were also rinsed with DCM to remove any products deposited on the surface. Rinse samples were found to contain no identifiable products and were combined with the

TABLE 1: Percent Yields (Carbon Basis) of Products from CPD Pyrolysis

		temperature (°C)											
		550	600	650	700	725	750	775	800	825[a]	850	900	950
cyclopentadiene	C_5H_6	100	90.7	88.0	84.9	52.8	45.7	27.5	16.8	8.93	0.850		
(dihydrofulvene)[b]	C_6H_8	0.310	0.989	0.415	0.792	0.877	0.873	0.736	0.341	0.005	0.001		
1,3-cyclohexadiene	C_6H_8	0.300	0.958	0.468	0.639	0.704	0.744	0.580	0.245	0.007	0.001		
benzene	C_6H_6	0.023	0.416	0.529	2.11	3.00	5.46	8.64	15.7	15.0	23.7	20.4	26.6
toluene	C_7H_8			0.074	0.244	0.685	1.48	2.43	3.55	4.50	5.76	2.13	0.114
(*p*-xylene)	C_8H_8					0.073	0.139	0.222	0.139	0.240	0.149		
(phenylethyne)	C_8H_8			0.075	0.000	0.015	0.071	0.191	0.255	0.462	0.492	0.515	0.188
styrene	C_8H_8				0.269	0.820	1.75	2.66	3.51	3.75	3.59	0.838	0.022
DCPD	$C_{10}H_{12}$	0.083	0.948	0.129	0.698	0.227	0.150	0.066	0.000	0.028			
indene	C_9H_8	0.031	0.205	0.980	5.52	6.53	11.8	14.7	21.7	15.1	8.81	1.86	0.063
2-methylindene	$C_{10}H_{10}$	0.002	0.003	0.071	0.168	0.343	0.269	0.155	0.104	0.004			
3-methylindene	$C_{10}H_{10}$	0.002	0.012	0.257	0.957	0.653	0.407	1.066	0.131				
(diydrobenzofulvene)	$C_{10}H_{10}$	0.001	0.004	0.142	0.679	0.361	0.261	0.070	0.050				
1,2-dihydronaphthalene	$C_{10}H_{10}$	0.005	0.032	0.304	1.303	1.191	1.142	0.818	0.410	0.114	0.003		
naphthalene	$C_{10}H_8$	0.004	0.038	0.617	2.77	4.72	9.25	14.7	23.7	28.6	30.6	20.4	13.7
1-methylnaphthalene	$C_{11}H_{10}$					0.006	0.029	0.066	0.052	0.164	0.121	0.084	0.002
2-methylnaphthalene	$C_{11}H_{10}$					0.006	0.028	0.065	0.075	0.176	0.117	0.054	0.001
biphenyl	$C_{12}H_{10}$							0.011	0.007	0.179	0.02	0.047	0.004
(ethenylnaphthalene)	$C_{12}H_{10}$									0.063	0.002	0.004	0.002
acenaphthylene	$C_{12}H_8$				0.001	0.017	0.075	0.169	0.301	0.586	0.938	1.51	1.59
acenaphthene	$C_{12}H_{10}$					0.001	0.004	0.007	0.000	0.012	0.002	0.004	
(1*H*-phenalene)	$C_{13}H_{10}$							0.006	0.003	0.011	0.002		
fluorene	$C_{13}H_{10}$						0.070	0.308	0.771	2.35	1.86	0.736	0.010
(benzindene)	$C_{13}H_{10}$						0.013	0.035	0.015	0.082	0.012	0.010	
(benzindene)	$C_{13}H_{10}$						0.012	0.032	0.011	0.069	0.007	0.008	
(benzindene)	$C_{13}H_{10}$						0.020	0.070	0.040	0.254	0.029	0.017	
(methylfluorene)	$C_{14}H_{12}$					0.000	0.018	0.080	0.081	0.089	0.017		
(methylfluorene)	$C_{14}H_{12}$					0.003	0.048	0.103	0.064	0.285	0.003		
(methylfluorene)	$C_{14}H_{12}$					0.006	0.076	0.219	0.292	0.404	0.022		
phenanthrene	$C_{14}H_{10}$					0.006	0.098	0.377	1.074	3.25	3.66	2.90	1.002
anthracene	$C_{14}H_{10}$					0.006	0.128	0.516	0.839	3.46	2.26	1.71	0.167
(4*H*-cyclopenta[*def*] phenanthrene)	$C_{15}H_{10}$						0.004	0.022	0.031	0.202	0.132	0.115	0.003
(methylphenanthrene)	$C_{15}H_{12}$						0.008	0.036	0.028	0.125	0.026		
(methylanthracene)	$C_{15}H_{12}$						0.009	0.038	0.035	0.171	0.051	0.010	
fluoranthene	$C_{16}H_{10}$								0.003	0.171	0.168	0.289	0.167
(acephenanthrylene)	$C_{16}H_{10}$								0.001	0.069	0.016	0.037	0.007
(aceanthrylene)	$C_{16}H_{10}$								0.001	0.009	0.023	0.104	0.023
benzo[*b*]fluorene	$C_{17}H_{12}$									0.069	0.002		
soot - assumed as all carbon										4.92	4.11	4.06	7.64

[a] Average of triplicate at 825 °C. [b] Parentheses denote compounds identified on the basis of published mass spectra.

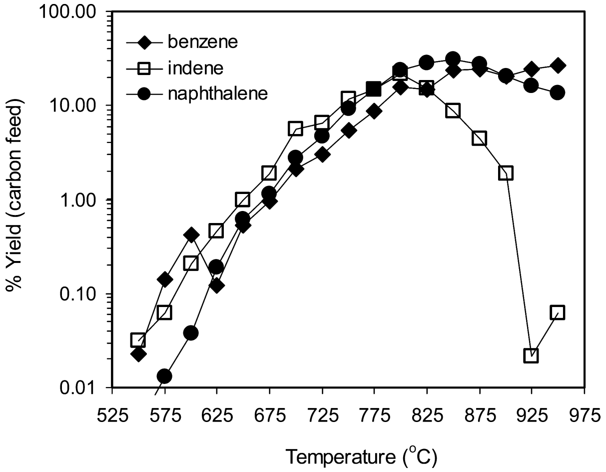


Figure 2. Yields of benzene, indene, and naphthalene from CPD pyrolysis.

DCM in the collection trap. The combined samples were filtered with a polytetrafluoroethylene membrane filter of 0.25 μL pore diameter by vacuum filtration to remove soot, defined as the DCM-insoluble fraction. Soot yields were determined gravimetrically. For calculation of total carbon recovery, soot was assumed to be pure carbon.

Filtered samples were analyzed by gas chromatography coupled with mass spectroscopy (GC/MS). The GC column employed was a HP-5MS capillary column with 30 m × 0.25 mm with a 0.25 μL film of cross-linked 5% siloxane. Occasionally, samples underwent the evaporative concentration process with nitrogen for better identification and detection of products with low concentrations. The GC column oven temperature was programmed as follows: an initial hold time of 2 min at 32 °C, 32 to 250 °C at a rate of 5 °C/min, 250 to 280 °C at a rate of 8 °C/min, and a final hold time of 3 min. Due to the high volatility of CPD and its coelution with the solvent, CPD concentrations were separately measured from gas samples by direct injection of the gas samples into the GC−MS column. Measurements of CPD in the gas sample were in triplicate at 600 °C.

Products were identified mainly by comparing the MS spectra and retention times with data for commercially available chemical standards including cyclopentene, 1,3-cyclohexadiene, 1-methylcyclopentadiene, 1-, 2- and 3-methylindene, 1,2-dihydrofulvalene, and naphthalene. Response factors were obtained through four dilutions of chemical standards. When standards were not available, product structures were identified on the basis of published MS spectra and elution order. Yields of the observed products were calculated with the response factors and peak areas expressed in a percent carbon input. For

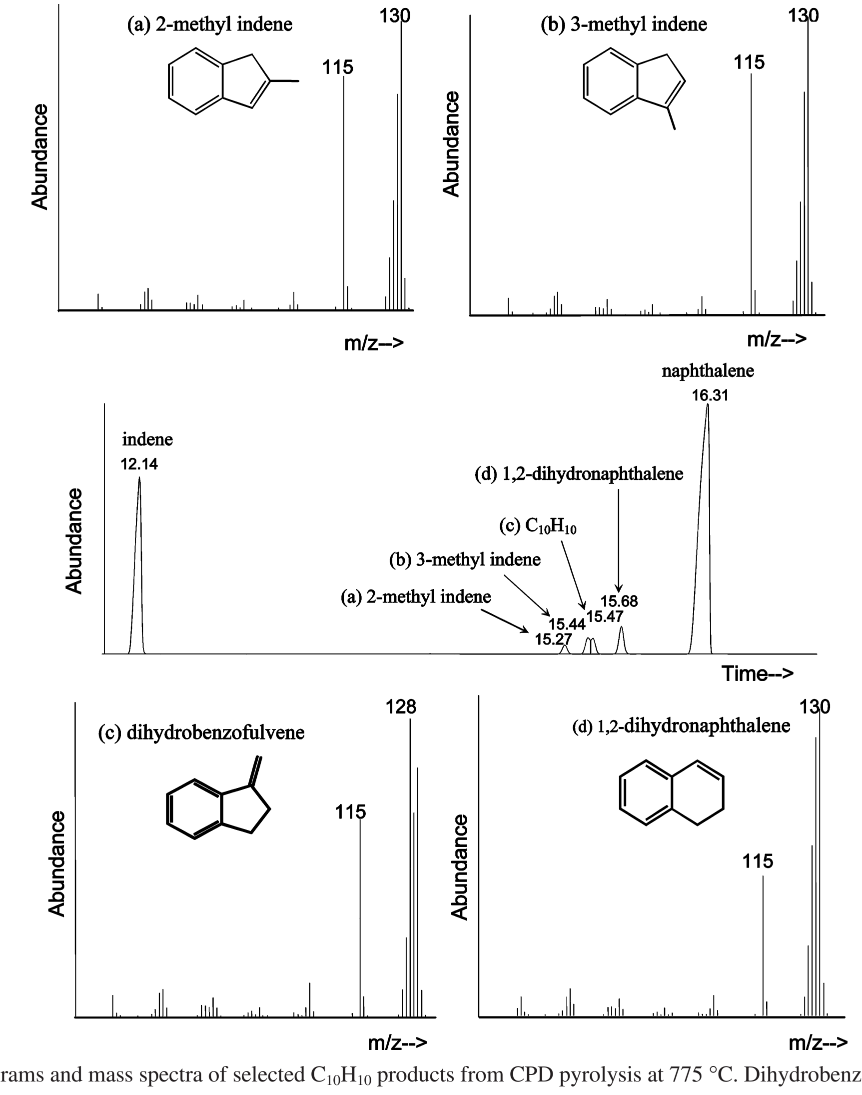


Figure 3. Ion chromatograms and mass spectra of selected $C_{10}H_{10}$ products from CPD pyrolysis at 775 °C. Dihydrobenzofulvene was not confirmed with chemical standard.

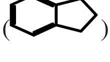
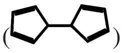
the products without standards, yields were estimated using response factors of compounds having similar structures.

Results and Discussion

Pyrolytic Product Yields. The yields of total carbon recovery, aromatic compounds, CPD, and soot over the temperature range 550−950 °C are shown in Figure 1 expressed as a percent of carbon fed to the reactor. The yields of observed products over the temperature range studied are reported in Table 1; soot was assumed to be pure carbon. Compounds enclosed in parentheses in Table 1 were identified on the basis of published mass spectra. Carbon recoveries of 80% and above were obtained for temperatures up to 850 °C. Lower carbon recoveries for temperatures higher than 875 °C are primarily attributed to unrecovered soot that could not be rinsed from the quartz tube wall. PAH product yields ranged from 2.7% of carbon input at 600 °C to 82% at 850 °C. The yields of CPD were greater than 85% up to 700 °C. Above 700 °C, CPD begins to react in significant amounts with more than 90% of the CPD reacted at 825 °C. Soot formation was observed starting at 850 °C and increasing with temperature.

The major products from CPD pyrolysis were benzene, indene, and naphthalene, and their yields are shown in Figure 2. The amount of indene produced exceeded that of naphthalene at temperatures lower than 775 °C. Between 775 and 900 °C, naphthalene was the main product, and above 900 °C, benzene formation becomes predominant. The high yields of benzene, indene, and naphthalene (more than 90% of total product yield) suggest that the self-recombination route of CPDyl radicals[24] and/or the CPDyl radical addition to CPD route[15,26−29] are dominant reaction channels until 850 °C. Overall, carbon is conserved in the conversion of 2 CPDs to naphthalene and 3 CPDs to indene and benzene. The latter route involves the formation of methyl radicals; methane was not measured in these experiments. At the lowest three temperatures studied (550, 575, and 600 °C), yields of C_6 compounds exceeded indene (C_9) yields by greater than a 9:6 ratio (Table 1); with yields expressed on a carbon basis, a 9:6 ratio corresponds to carbon conservation via 3 CPDs being converted to benzene and indene. Butler and Glassman[29] noted higher methane concentrations than expected in CPD combustion experiments, consistent with our finding of higher C_6 product yields than expected at the lowest temperatures. We did not measure methane in these experiments, however. At 600 °C and below, product yields were very low and impurities in the DCPD feed (99.9% purity) might account for the excess in C_6 product yields. At 725 °C and above, the lack of full carbon recovery might be due to methane production.

The observation of high yields of benzene, indene, and naphthalene from CPD pyrolysis and the crossover of indene and naphthalene yields around 775 °C appear to be consistent with the computational studies.[15,26−28,31] However, the specific intermediates leading to indene and naphthalene from CPD in the proposed pathways were not observed over the temperatures studied. Ion chromatograms and mass spectra of observed $C_{10}H_{10}$ compounds from CPD pyrolysis are shown in Figure 3. On the basis of the elution times and mass spectra of available standards, three of the observed $C_{10}H_{10}$ compounds were identified as 2- and 3-methylindenes and 1,2-dihydronaphthalene.

Although one $C_{10}H_{10}$ compound, denoted as (c) in Figure 3, was not identified by chemical standard, the mass spectrum and elution time of this compound relative to methyl indenes suggested that this compound is dihydrobenzofulvene (), not dihydrofulvalene (), a precursor for naphthalene formation from CPD in the proposed mechanism suggested by Melius et al.[24] The abundance order of principal *m*/*z* peaks associated with this hydrocarbon (128 > 130 > 129) in the mass spectrum is not consistent with the published order of principal *m*/*z* peaks in a dihydrofulvalene (129 > 128 > 130).[32] Moreover, this hydrocarbon does not have a distinctive signature of the dihydrofulvalene with a big half-ion peak at 65 *m*/*z* whereas both 1,1- and 1,2-biindenyl containing a dihydrofulvalene moiety have a distinguished half-ion peak at 115 *m*/*z*.[33]

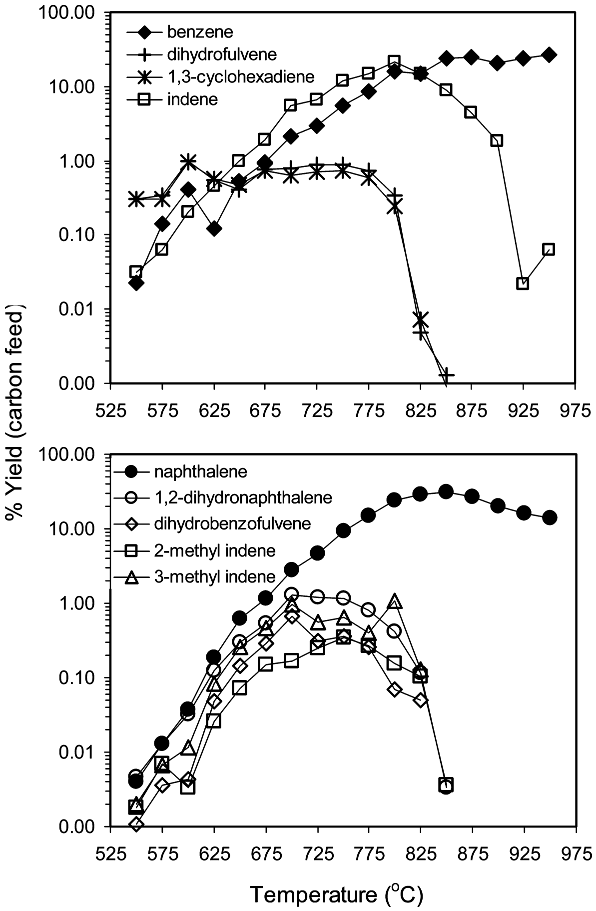


Figure 4. Yields of major aromatic products and their derivatives from CPD pyrolysis.

Yields of benzene, indene, and naphthalene and their derivatives from CPD pyrolysis are compared in Figure 4. Yields of 1,3-cyclohexadiene and another C_6H_8 compound, possibly dihydrofulvene, were greater than the yield of benzene below 675 °C. Similarly, the ratio of 1,2-dihydronaphthalene to naphthalene was highest at low temperatures and decreased with increasing temperature. These results indicate that cyclohexadiene and dihydronaphthalene might be intermediates for benzene and naphthalene formation, respectively. On the other hand, indene yield was much greater than yields of methylindenes and dihydrobenzofulvene at low temperatures, suggesting that these products might be formed from indene. Thus, our results suggest that, in addition to the CPD-to-naphthalene mechanism,[24] naphthalene might be also formed from indene via methylation followed by a ring expansion of methylindenes, analogous to the conversion of the methylcyclopentadienyl radical to benzene.[34,35]

Minor products observed include toluene, styrene, fluorene, phenanthrene, anthracene, and acenaphthylene (Table 1). Trace amounts of xylene, phenylethyne, methyl- and ethylnaphtha-

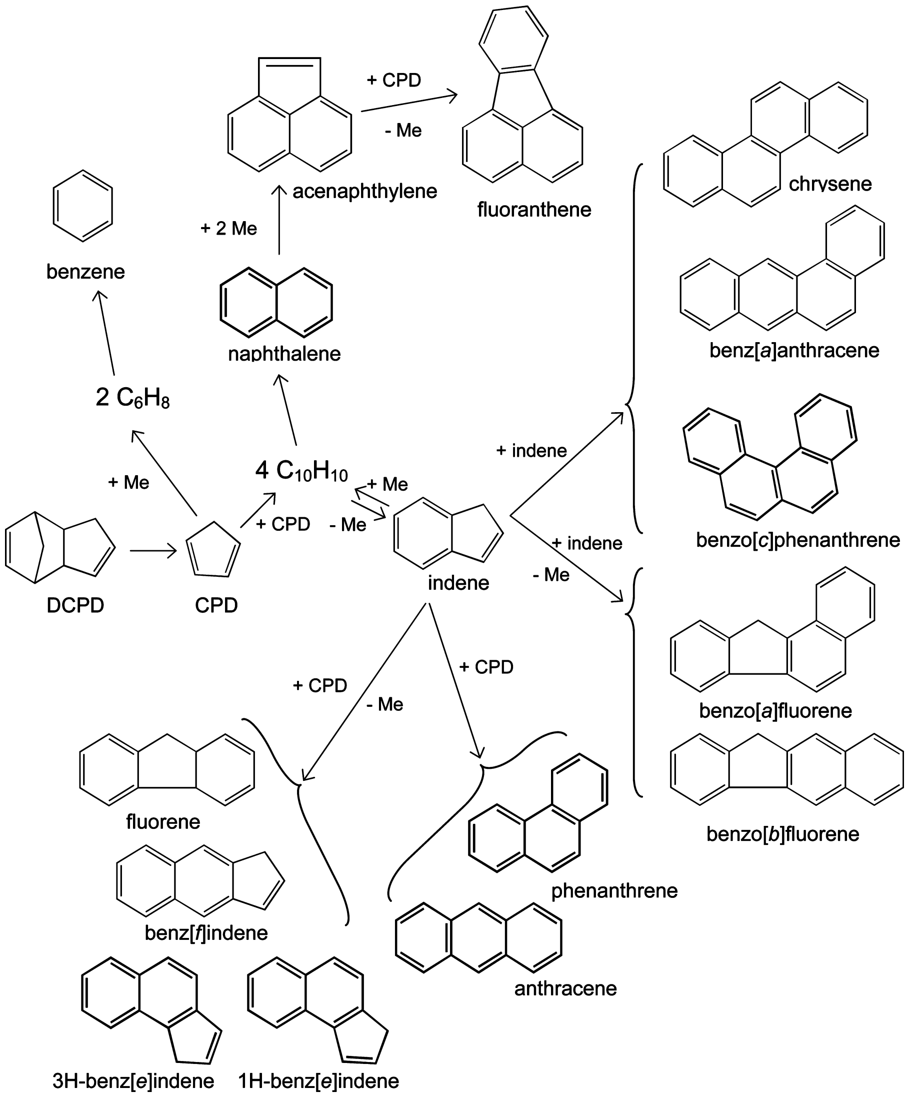


Figure 5. Observed PAH growth from CPD pyrolysis.

lenes, and fluoranthene were also found at temperatures above 750 °C. Yields of most of the minor products, except acenaphthylene, reached a maximum between 825 and 850 °C and then decreased. Phenanthrene reached a maximum at 850 °C with a yield of 3.5% carbon feed and declined, whereas anthracene reached a maximum at 825 °C with the yield of 3.3% and declined. The maximum yield of fluorene was also achieved at 825 °C. Fluorene, phenanthrene, and anthracene have been proposed to be products of the reaction between CPD and indene,[26,28] which is supported here by the fact that their yields are proportional to the indene yield over the temperature range studied.

Toluene, styrene, and other C_8 species appear to be formed from the reactions involving CPD, benzene, and acyclic fragments. Unlike other minor products, acenaphthylene yield keeps increasing as temperature increases. Acenaphthylene has been suggested to be an important product supporting PAH growth by the carbon addition.[7,16] As naphthalene becomes a dominant product and more acyclic fragments are available at high temperatures, acenaphthylene is expected to be formed from the addition of acetylene to naphthalene,[11,12] which is further supported by the observation of ethenylnaphthalene. The observation of these products suggests that growth via carbon fragments (e.g., the HACA mechanism) likely becomes an important route for PAH growth at high temperatures.

PAH Growth from CPD: Comparison of Experimental and Computational Results. Observed PAH formation pathways from CPD pyrolysis, including our previous CPD−indene experimental results,[26−28] are summarized in Figure 5.

Computational results suggest that the CPDyl radical recombination route leading to naphthalene competes with the intramolecular addition route of the CPDyl radical to CPD, leading to indene at low and medium temperatures under pyrolytic conditions where the contribution of routes involving carbon fragments is expected to be low.[15,31] With respect to the naphthalene production from CPD, the calculated reaction rate constants at the high-pressure limit indicate that the CPD-to-naphthalene mechanism of Melius et al.[24] is the major contributor to the naphthalene production at low combustion temperatures ($T < 1000$ K) whereas an alternative C−C bond scission route suggested by Wang et al.[15] becomes important only at higher temperatures.[30,31]

The observed high selectivity of indene, benzene, and naphthalene and the observation of similar, though not identical, intermediates as those proposed support the computational results. Failure to observe the computationally predicted 4- and 7-methylindene and 9,10-dihydronaphthalene intermediates might be due to rearrangement of these compounds to more stable compounds that were observed; namely, 2- and 3-methylindenes and 1,2-dihydronaphthalene. The crossover of indene and naphthalene yields was observed around 775 °C, much lower than that predicted by the computational studies.[15,24,26−28] One possible explanation of this discrepancy is the suggestion of Wang et al.[15] that the inclusion of H abstraction reaction in the calculation would greatly improve the formation rate of naphthalene.

The loss of a methyl group in the CPD-to-indene pathway[26−28] leads to methylcyclopentadiene formation, ring expansion to form the observed cyclohexadienes, and then dehydrogenation to form benzene.[34,35] Similarly, naphthalene might also be formed from indene via the observed methylindene and dihydronaphthalene intermediates. Further PAH growth by addition of cyclopentadienyl moieties was observed. Reaction of indene and CPD produces fluorene, phenanthrene, and anthracene.[26] Reaction of two indenes produces benzo[*a*]fluorene, benzo[*b*]fluorene, chrysene, benz[*a*]anthracene, and benzo[*c*]phenanthrene.[27] CPD−acenaphthylene reaction produces fluoranthene.[16]

Conclusions

High selectivity for benzene, indene, and naphthalene products were observed in CPD pyrolysis over the temperature range 550−950 °C. A crossover of indene and naphthalene yields was observed, as suggested in the computational studies. Although not all of the intermediates expected on the basis of computational studies were detected, the experimental results support the pyrolytic growth of PAH via CPDyl addition pathways at temperatures below 900 °C.

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Supporting Information Available: A schematic diagram of the experimental apparatus; axial temperature profiles of the quartz tube reactor. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) D'Anna, A.; Violi, A.; D'Alessio, A. *Combust. Flame* **2000**, *121*, 418–429.

(2) Violi, A.; Sarofim, A. F.; Truong, T. N. *Combust. Flame* **2001**, *126*, 1506–1515.

(3) Durant, J. L.; Busby, W. F.; Lafleur, A. L.; Penman, B. W.; Crespi, C. L. *Mutat. Res.* **1996**, *371*, 123–157.

(4) Durant, J. L.; Lafleur, A. L.; Busby, W. F.; Donhoffner, L. L.; Penman, B. W.; Crespi, C. L. *Mutat. Res.* **1999**, *446*, 1–14.

(5) Violi, A.; D'Anna, A.; D'Alessio, A.; Sarofim, A. F. *Chemosphere* **2003**, *51*, 1047–1054.

(6) Violi, A.; D'Anna, A.; D'Alessio, A. *Chem. Eng. Sci.* **1999**, *54*, 3433–3442.

(7) Violi, A. *J. Phys. Chem. A* **2005**, *109*, 7781–7787.

(8) Homann, K. H.; Wagner, H. G. *Proc. Combust. Inst.* **1967**, *11*, 371–376.

(9) Crittenden, B. D.; Long, R. *Combust. Flame* **1973**, *20*, 359–368.

(10) Bockhorn, H.; Fetting, F.; Wenz, H. W. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 1067–1073.

(11) Frenklach, M.; Clary, D. W.; Cardiner, W. C.; Stein, S. E. *Proc. Combust. Inst.* **1984**, *20*, 887–901.

(12) Cole, J. A.; Bittner, J. D.; Longwell, J. P.; Howard, J. B. *Combust. Flame* **1984**, *56*, 51–70.

(13) Westmoreland, P. R.; Dean, A. M.; Howard, J. B.; Longwell, J. P. *J. Phys. Chem.* **1989**, *93*, 171–180.

(14) Marinov, N. M.; Pitz, W. J.; Westbrook, C. K.; Castaldi, M. J.; Senkan, S. M. *Combust. Sci. Technol.* **1996**, *116*, 117–211.

(15) Wang, D.; Violi, A.; Kim, D. H.; Mullholland, J. A. *J. Phys. Chem. A* **2006**, *110*, 4719–4725.

(16) Wang, D.; Violi, A. *J. Org. Chem.* **2006**, *71*, 8365–8371.

(17) Marinov, N. M.; Pitz, W. J.; Westbrook, C. K.; Vincitore, A. M.; Castaldi, M. J.; Senkan, S. M.; Melius, C. F. *Combust. Flame* **1998**, *114*, 192–213.

(18) Lamprecht, A.; Atakan, B.; Kohse-Höinghaus, K. *Proc. Combust. Inst.* **2000**, *28*, 1817–1824.

(19) Gomez, A.; Sidebotham, G.; Glassman, I. *Combust. Flame* **1984**, *58*, 5845–5857.

(20) Spielmann, R.; Cramers, C. A. *Chromatographia* **1972**, *5*, 295–300.

(21) Manion, J.; Louw, R. *J. Phys. Chem.* **1989**, *93*, 3563–3574.

(22) Friderichsen, A. V.; Shin, E.-J.; Evans, R. J.; Nimlos, M. R.; Dayton, D. C.; Ellison, G. B. *Fuel* **2001**, *80*, 1747–1755.

(23) Miller, J. A. *Proc. Combust. Inst.* **1996**, *26*, 461–480.

(24) Melius, C. F.; Colvin, M. E.; Marinov, N. M.; Pitz, W. J.; Senkan, S. M. *Proc. Combust. Inst.* **1996**, *26*, 685–692.

(25) Richter, H.; Benish, T. G.; Mazyar, O. A.; Green, W. H.; Howard, J. B. *Proc. Combust. Inst.* **2000**, *28*, 2609–2618.

(26) Mulholland, J. A.; Lu, M.; Kim, D. H. *Proc. Combust. Inst.* **2000**, *28*, 2593–2599.

(27) Lu, M.; Mulholland, J. A. *Chemosphere* **2001**, *42*, 625–633.

(28) Lu, M.; Mulholland, J. A. *Chemosphere* **2004**, *55*, 605–610.

(29) Butler, R. G.; Glassman, I. *Proc. Combust. Inst.* **2009**, *32*, 395–402.

(30) Kislov, V. V.; Mebel, A. M. *J. Phys. Chem. A* **2007**, *111*, 9532–9543.

(31) Kislov, V. V.; Mebel, A. M. *J. Phys. Chem. A* **2008**, *112*, 700–716.

(32) Beach, D. B. *IBM J. Res. Dev.* **1990**, *34*, 795–805.

(33) Herring, A. M.; McKinnon, J. T.; Petrick, D. E.; Gneshin, K. W.; Filley, J.; McCloskey, B. D. *J. Anal. Appl. Pyrol.* **2003**, *66*, 165–182.

(34) Madden, L. K.; Mebel, A. M.; Lin, M. C.; Melius, C. F. *J. Phys. Org. Chem.* **1996**, *9*, 801–810.

(35) Dubnikova, F.; Lifshitz, A. *J. Phys. Chem. A* **2002**, *106*, 8173–8183.

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