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Aromatic hydrocarbon growth from indene $\stackrel{\text{tr}}{\sim}$

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Abstract

Aromatic hydrocarbon growth from indene (C_9H_8), which contains the five-membered ring cyclopentadienyl moiety, was investigated experimentally in a 4 s flow reactor over a temperature range 650–850°C. Major products observed were three $C_{18}H_{12}$ isomers (chrysene, benz[*a*]anthracene and benzo[*c*]phenanthrene), two $C_{17}H_{12}$ isomers (benzo[*a*]fluorene and benzo[*b*]fluorene), and two $C_{10}H_8$ isomers (naphthalene and benzofulvene). Reaction pathways to these products are proposed. Indenyl radical addition to indene produces a resonance-stabilized radical intermediate which further reacts by one of two routes. Rearrangement by intramolecular addition produces a bridged structure that leads to the formation of $C_{17}H_{12}$ and $C_{10}H_8$ products. Alternatively, β scission produces biindenyl, which leads to the formation of $C_{18}H_{12}$ products by a ring condensation mechanism analogous to that proposed for cyclopentadiene-to-naphthalene conversion. Temperature dependencies of both the partitioning between these two routes and the product isomer distributions are consistent with thermochemical modeling using semi-empirical molecular orbital methods. The results further illustrate the role of resonance-stabilized radical rearrangement in aromatic growth and condensation of systems with cyclopentadienyl moieties. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Formation of polycyclic aromatic hydrocarbons (PAHs) and soot in flames continues to be studied due to the complexity of the reaction mechanisms. These products of incomplete combustion are of interest because several PAHs are known to be mutagens and carcinogens and exposure to fine soot particles, which can carry PAHs deep into the lung, has been linked to increased rates of morbidity and mortality. Early study

of PAH formation and growth in flames focussed on acetylene addition pathways (Frenklach et al., 1984). More recently, the importance of resonance-stabilized, or neutral, cyclopentadienyl radicals (C_5H_5) in aromatic ring formation has been studied. Fuels containing cyclopentadienyl moieties have high sooting tendencies (McEnally and Pfefferle, 1998). Cyclopentadienyl radicals are also produced in flames by phenoxy radical ring contraction (Manion and Louw, 1989). Unimolecular decomposition of cyclopentadienyl radical at high temperatures produces acetylene and resonance-stabilized propargyl radical (Roy et al., 1998) which contribute to aromatic growth. Cyclopentadienyl radicals decompose slowly, however, due to their stability; therefore, they can contribute to PAH growth directly by combining to form naphthalene (Manion and Louw, 1989; Castaldi et al., 1996; Marinov et al., 1996; Melius et al., 1996).

While there has been detailed study of the chemical mechanism of naphthalene formation from cyclopent-

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adiene (Melius et al., 1996), there has been little study of the reactivity of its benzo derivatives, such as indene. Laskin and Lifshitz (1998) studied the thermal decomposition of indene, but not carbon growth by indenyl radical addition. McEnally and Pfefferle (1998) studied naphthalene formation from indene and methane, but did not report on higher molecular weight products. In this paper, we present experimental and computational results on aromatic growth from indene. We extend the cyclopentadiene-to-naphthalene mechanism of Melius to the conversion of indene (C_9H_8) to $C_{18}H_{12}$ isomers that contain four six-membered rings. In addition, a second reaction pathway is proposed for the formation of C₁₇H₁₂ and C₁₀H₈ products from indene. Semi-empirical molecular orbital modeling results are presented to explain the temperature dependence of partitioning between the two pathways as well as the distribution of C₁₈H₁₂ isomer products.

2. Naphthalene formation from cyclopentadienyl radicals

2.1. Reaction mechanism

Melius et al. (1996) studied cyclopentadienyl radical reactions using the quantum chemical BAC-MP2 and BAC-MP4 methods. After investigating reaction energies of alternative routes, they proposed a nine-step reaction mechanism for the conversion of two cyclopentadienyl radicals to naphthalene via rearrangements involving three-membered ring closing and opening of resonance-stabilized radicals (Fig. 1). Dimerization of cyclopentadienyl radicals yields 9,10-di-



Fig. 1. Reaction mechanism proposed by Melius et al. (1996) for the conversion of two cyclopentadienyl radicals to naphthalene (9) via 9,10-dihydrofulvalene (1) and 1,10-dihydrofulvalene (2).

hydrofulvalene (1), which rearranges to form the more stable 1,10-dihydrofulvalene (2). Loss of H-atom from the 10-carbon site produces a tertiary, resonance-stabilized radical (3). Isomerization by 1,3-H shift produces (4), which undergoes three-membered ring closure to form (5). Ring opening by β scission of a C–C bond produces a six-membered ring (6). Reactions producing (5) and (6) are repeated to produce (7) and (8), respectively, converting a second five-membered ring to sixmembered ring. In the final step, β scission yields naphthalene (9) and H-atom.

2.2. Comparison of heats of reaction calculated by Ab initio and semi-empirical methods

Heats of formation of stable intermediates calculated by Melius using the ab initio BAC-MP2 method are compared with those calculated using semi-empirical methods in Fig. 2. Three semi-empirical methods based on the neglect of diatomic differential overlap approximation were evaluated: modified neglect of diatomic overlap (MNDO), Austin model 1 (AM1) and parametric method 3 (PM3). While the absolute values of the heats of formation calculated using the ab initio BAC-MP2 method and three semi-empirical methods differ significantly, the relative energy levels, or heats of reaction, are similar (Table 1). For example, fulvalene formation is not favored thermodynamically by any of the methods (Fig. 2). Biggest discrepancies between semi-empirical and BAC-MP2 heats of reaction are for the first and last steps: the combination of two cyclopentadienyl radicals to form 9,10-dihydrofulvalene (1) and the formation of naphthalene (9) by C–H bond β scission. Overall, PM3 and AM1 heats of reaction correlate well with the BAC-MP2 values (0.95 and 0.92 Rsquared values, respectively); the MNDO R-squared value is 0.83.

Modeling of the cyclopentadiene system demonstrates that the formation of five-membered ring dimers and their subsequent rearrangement to ortho-fused sixmembered ring structures via three-membered ring intermediates is a plausible mechanism for aromatic growth. Here, we apply this mechanism to indene, a benzo derivative of cyclopentadiene. Experiments were performed to test the hypothesis that aromatic growth from indene would occur by biindenyl formation and rearrangement to $C_{18}H_{12}$ products that contain four ortho-fused six-membered rings. Due to the large number of atoms in this system, computational investigation using ab initio methods was not feasible. Therefore, semi-empirical molecular orbital methods were used to estimate reaction path thermodynamic barriers. We have also used semi-empirical methods to estimate transition state barriers; these results are being reported elsewhere.



reaction coordinate

Fig. 2. Thermodynamic energy diagram for the conversion of two cyclopentadienyl radicals to naphthalene (9). Structures are shown in Fig. 1, with the exception of fulvalene ($C_{10}H_8$). Heats of formation of stable and radical species, but not transition states, were calculated using the BAC-MP2 ab initio method of Melius et al. (1996) and the MNDO, AM1 and PM3 semi-empirical methods.

Table 1 Standard heats of reaction for cyclopentadiene-to-naphthalene mechanism

	$\Delta H_{r,298}^{\circ}$, kcal/mol						
	BAC-MP2 ^a	MNDO	AMI	PM3			
$2 C_5 H_5 \rightarrow (1)$	-52.0	-22.9	39.7	-38.8			
$(1) \rightarrow (2)$	-2.2	-7.3	-3.6	-4.5			
$(2) \rightarrow (3) + H$	62.6	51.3	59.3	60.1			
$(3) \rightarrow (4)$	17.2	16.2	17.7	15.3			
$(4) \rightarrow (5)$	5.3	10.2	12.8	12.1			
$(5) \rightarrow (6)$	-18.4	-20.8	-33.0	-24.6			
$(6) \rightarrow (7)$	13.1	5.5	13.7	12.7			
$(7) \rightarrow (8)$	-33.9	-32.7	-41.7	-33.3			
$(8) \rightarrow (9) + H$	18.9	42.5	35.4	33.7			

^a BAC-MP2 data from Melius et al. (1996).

3. Experimental methods

A laminar flow, isothermal quartz tube reactor was used to study indene pyrolysis chemistry. Indene vapor was generated by loading 20 µl of indene (99% purity) into a glass bulb heated to 140°C (40°C below the indene boiling point), and then passing through helium carrier gas at a rate of 390 standard ml/min until all of the indene was vaporized and delivered to the reactor through heated transport lines. The gas stream containing 0.2 mol% (nominal) indene vapor had a 4 s residence time in the reactor. An experiment took approximately 5 min to complete, with the entire product stream immediately quenched at the outlet of the reactor and sampled. Gas samples taken during an experiment demonstrated that the indene vapor concentration delivered to the reactor was constant over 90% of the experiment.

Unreacted indene, aromatic products and soot were collected on an inert filter (0.2 µm) followed by two icecooled dichloromethane (DCM) impingers in series. Filter, impinger and rinse samples were combined and soot, defined as the DCM-insoluble fraction, was separated by vacuum filtration and measured gravimetrically. Samples were then analyzed using a Varian 2000 GC/ MS with DB5-ms capillary column and a Hewlett– Packard 1050 HPLC with UV-vis diode array detector. Products were identified and quantified using chemical standards, except for biindenyl and methyl benzofluorene products which were identified on the basis of elution order and spectral data and quantified using GC/ MS response factors for compounds of similar size and structure.

A temperature range 650–850°C was studied, the range over which 90% of the indene was reacted. Below 650°C, thermal decomposition of indene was not observed. Above 850°C, ring fragmentation pathways became significant. Two to four experiments were performed at each temperature. A total carbon balance was calculated for each experiment, with results ranging from 100% for the lower temperature experiments to 85% at 850°C.

4. Results and discussion

4.1. Pyrolysis product yields

Yields of unreacted indene, total aromatic products, and soot are shown in Fig. 3 for the temperature range 650–850°C. Data are presented on a percent carbon feed basis, with soot assumed to be 100% carbon. Also shown is total carbon recovery. Average values are indicated by the points, with the range of values from three experiments shown at 825°C. At 650°C, less than 3% of the indene was reacted; at 850°C, about 90% of the indene was reacted. Total aromatic product and soot yields increased with temperature. Unrecovered carbon, which did not exceed 15% for any experiment, was primarily due to unrecovered soot that could not be rinsed from the from the quartz tube wall at the point of quenching. For temperatures above 850°C, low carbon recovery and a broad range of aromatic products were observed, indicative of indene ring fragmentation. Yields of aromatic product groups, representing over 99% of the total aromatic product yield, are shown in Fig. 4. As expected based on the cyclopentadiene-tonaphthalene mechanism, three $C_{18}H_{12}$ isomers were found as major products, and both 1,1- and 1,2-biindenyls ($C_{18}H_{14}$) were observed. Two $C_{10}H_8$ isomers, two $C_{17}H_{12}$ isomers (benzofluorenes), and two additional $C_{18}H_{14}$ isomers that were identified as methyl benzofluorenes were also observed. Impurities in the indene reactant are likely responsible for the 1% yields of $C_{10}H_8$ species at low temperatures. At 750°C and above, the $C_{10}H_8$ and $C_{17}H_{12}$ product yields were of similar magnitude, suggesting that $C_{10}H_8$ and $C_{17}H_{12}$ products may



Fig. 3. Total carbon recovery and yields of unreacted indene, total aromatic products and soot from indene pyrolysis. Average values are shown, with a range of values given at 825°C.



Fig. 4. Aromatic product yields from indene pyrolysis. In parentheses, the numbers of isomers detected are given. Average yields are shown, with a range of values indicated at one temperature.

have been formed together from three indene molecules. The temperature dependence of the biindenyl and the methyl benzofluorene yields suggests that these compounds are intermediates to $C_{18}H_{12}$ products and $C_{17}H_{12}/C_{10}H_8$ products, respectively.

Isomer fractions for $C_{10}H_8$, $C_{17}H_{12}$ and $C_{18}H_{12}$ products are shown in Fig. 5. In the top panel, the $C_{10}H_8$ product isomer distribution shows a decreasing benzofulvene-to-naphthalene ratio with increasing temperature. McEnally and Pfefferle (1998) have proposed a route of indene conversion to naphthalene via benzofulvene, which is consistent with our results. The single carbon required for indene conversion to benzofulvene is likely generated by the formation of two $C_{17}H_{12}$ isomers, benzo[*a*]fluorene and benzo[*b*]fluorene, from methyl benzofluorene decomposition. Benzo[*b*]fluorene was produced in greater quantities than benzo[*a*]fluorene by a factor of 3 and more (middle panel, Fig. 5), consistent with the thermodynamic properties of these isomers.

Three of the five ortho-fused $C_{18}H_{12}$ isomers were produced: chrysene, benz[*a*]anthracene and benzo[*c*]phenanthrene (bottom panel, Fig. 5). Two other $C_{18}H_{12}$ isomers, triphenylene and naphthacene, were not found. The relative yields of the three isomers that were formed are consistent with their relative stabilities, with chrysene, the most stable isomer, produced in highest yield and benzo[*c*]phenanthrene, the least stable isomer, produced in lowest yield.

4.2. Reaction pathways

Reaction pathways are proposed to account for the observed aromatic products. The nine-step cyclopent-

adiene-to-naphthalene mechanism shown in Fig. 1 is extended to the indene system, with analogous numbering of reaction intermediates shown in Fig. 6. In the indene mechanism, four routes are possible for the second ring closure step producing three-membered ring intermediates (7). Subsequent ring opening produces (8), followed by H-atom loss to produce the three observed $C_{18}H_{12}$ isomers (9); benz[*a*]anthracene has a reaction path degeneracy of 2, consistent with its lack of symmetry. The fact that only these three $C_{18}H_{12}$ isomers were observed supports the proposed mechanism.

A second pathway of aromatic growth is proposed to explain the formation of $C_{10}H_8$ and $C_{17}H_{12}$ products. Instead of indenyl radical-radical combination to form 1,1-biindenvl (1), indenvl radical addition to the nonaromatic indene double bond can occur. Addition is favored at the 2-carbon site of indene such that a resonance-stabilized radical is produced. This radical can undergo either intramolecular addition to form a bridged radical intermediate (route A) or β scission of a C-H bond to produce 1,2-biindenyl (route B). The latter route proceeds to the $C_{18}H_{12}$ isomer products as before. The bridged radical intermediate, on the other hand, can rearrange to form methyl benzo[b]fluorenes. Subsequent loss of CH₂ results in the formation of benzo[b]fluorene, which can isomerize to form benzo[a]fluorene. Addition of CH₂ to indene leads to the formation of benzofulvene, which rearranges to form naphthalene.

Reaction path thermodynamic energies calculated using the PM3 method are shown in Fig. 7. Reaction enthalpies favor the formation of benzofluorene products via the bridged intermediate (A) over the formation of $C_{18}H_{12}$ products via biindenyl (B). Heats of reaction for indenyl radical conversion to $C_{18}H_{12}$ products is very



Fig. 5. Isomer fractions of $C_{10}H_8$, $C_{17}H_{12}$ and $C_{18}H_{12}$ products from indene pyrolysis. Average values are shown, with a range of values indicated at one temperature.



Fig. 6. Proposed reaction mechanism for the formation of $C_{10}H_8$, $C_{17}H_{12}$ and $C_{18}H_{12}$ products from indene. Boxes designate compounds that were measured in the experiment.

similar to that of cyclopentadienyl radical conversion to naphthalene, as expected. The reaction step that determines which $C_{18}H_{12}$ product isomer is formed is the rearrangement of intermediate (6) to produce (7). Route

(a), which leads to chrysene, is favored by 9.7 kcal/mol over route (c), which leads to benz[*a*]anthracene, and by 15 kcal/mol over route (b), which leads to benzo[*c*]phenanthrene. Route (d) has the highest thermodynamic



reaction coordinate

Fig. 7. PM3 thermodynamic energy diagram for the formation of $C_{18}H_{12}$ products and methyl benzofluorenes from indene. Labels refer to structures shown in Fig. 6.

energy barrier. Effects of reaction temperature on the partitioning between benzofluorene and $C_{18}H_{12}$ product pathways and the $C_{18}H_{12}$ isomer distribution are examined in the following sections.

4.3. Temperature dependence of partitioning between benzofluorene and $C_{18}H_{12}$ product pathways

The ratio of the total $C_{18}H_{12}$ product yield to the total benzofluorene product yield, shown in Fig. 8, demonstrates that reaction path (A) is favored at low temperatures and reaction path (B) is favored at high temperatures. The results are consistent with kinetic parameters for path (A) that are 30 kcal/mol lower in enthalpy (favorable) and 30 cal/mol/K lower in entropy (unfavorable) than for path (B). Thermodynamically, reaction (A) is found to be less endothermic than reaction (B) by 48 kcal/mol (Fig. 7), as calculated by the PM3 method, and path (A) is expected to have an unfavorable entropy of reaction due to loss of internal rotation. This entropy loss is estimated to be 8 cal/mol/K using the method of Pitzer (1953) for free internal rotation and modified for hindered rotation (Mulholland et al., 1993). Transition state calculations are needed to assess actual kinetic barriers. The difference in kinetic enthalpy barriers is expected to be smaller than the difference in thermodynamic heats of reaction since the activation energy of reaction (A) should have a larger electronic component than that of reaction (B). The difference in entropy barriers is expected to be greater than that due only to the loss of internal rotation entropy in reaction (A) since this reaction also involves a strained bridged structure.

4.4. Temperature dependence of $C_{18}H_{12}$ isomer product distribution

To evaluate the degree to which thermodynamic barriers control the rate of formation of C₁₈H₁₂ product isomers for the affine set of reactions proposed, thermodynamic properties of the C₁₈H₁₂ products and radical intermediates were calculated. Differences in isomer heats of formation and symmetry numbers, whose ratios represent statistical factors (Bishop and Laidler, 1964), affect the thermodynamic distribution of isomers. In Table 2, experimental measurements of the heats of formation of three-ring and four-ring ortho-fused PAHs are compared with calculated values using ab initio and semi-empirical methods. While the BAC-MP2 ab initio method is clearly superior in predicting absolute heat of formation, the AM1 and PM3 semi-empirical methods predict differences in the heats of formation of these isomers that agree well with the experimental differences.

Experimental and calculated thermodynamic isomer fractions for $C_{18}H_{12}$ products are compared in Fig. 9. At high temperatures and high indene conversion, the experimental distribution appears to approach a thermodynamic distribution of products. At low temperature and low conversion, chrysene is favored by an amount consistent with the thermodynamic barriers for the formation of radical intermediates (7). The range in enthalpies of the intermediates is greater than that of the products due largely to differences in aromaticity of these intermediates, as shown in Fig. 6 by the number six π -electron systems in each of the structures. At low temperatures, when the relative rates of intermediate (7) formation are controlling, and at high temperatures, when the relative rates of $C_{18}H_{12}$ product (9) formation



Fig. 8. Ratio of total C₁₈H₁₂ product yield to total benzofluorene product yield. The curve represents a fit to the data.

	Sym.	$\Delta \mathrm{H_{f,298}}^{\circ}$, kcal/mol					
		Exp ^a	BAC-MP2 ^b	MNDO	AMI	PM3	
Phenanthrene	2	49.5	47.5	55.7	57.4	55.0	
Anthracene	4	54.4	54.4	58.8	62.9	61.7	
Triphenylene	6	61.9	60.1	76.9	75.5	68.3	
Chrysene	2	62.8	61.4	75.2	76.0	70.9	
Benz[a]anthracene	1	69.5	64.6	75.1	78.4	74.7	
Benzo[c]phenanthrene	2	69.8	65.2	79.8	81.0	77.6	
Naphthacene	4	72.3	75.2	81	87.0	84.4	

Table 2 Symmetry numbers and standard heats of formation for $C_{14}H_{10}$ and $C_{18}H_{12}$ compounds

^a Experimental data from TRC Thermodynamic Table (1995) and Cox and Pilcher (1970).

^b BAC-MP2 data from Melius et al. (1996).



Fig. 9. Thermodynamic isomer distributions of $C_{18}H_{12}$ products (solid lines), calculated by BAC-MP2, AM1 and PM3 methods, and radical intermediates (dashed lines – PM3). Experimental data are shown by symbols: chrysene – circles; benz[*a*]anthracene – triangles; benz[*c*]phenanthrene – squares. Radical intermediates are those labeled (7) in Fig. 6.

are controlling, the respective thermodynamic barriers appear to predict the experimental results. Consistent with this result, Melius found the activation energies, calculated using the BAC-MP2 method, of the two analogous cyclopentadiene-to-naphathalene reactions to be the same as the thermodynamic barriers for these reactions.

5. Conclusion

Our results offer further support the importance of resonance-stabilized radicals in aromatic and soot growth mechanisms. We have extended a mechanism of naphthalene formation from cyclopentadiene to the formation of three $C_{18}H_{12}$ isomers from indene, involving the conversion of five-membered ring moieties

to six-membered ring structures. In addition, we propose a second pathway to explain the formation of benzofluorene products which retain one cyclopentadiene moiety and provide a C_1 fragment that adds to indene to produce naphthalene via benzofulvene. Effects of temperature on the overall relative rates of the two mechanisms and on the distribution of $C_{18}H_{12}$ isomer products are shown to be consistent with thermodynamic properties estimated by semi-empirical quantum chemical methods.

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