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Abstract

The quantum chemical BAC-MP4 and BAC-MP2 methods have been used to investigate the reaction mechanisms leading to polycyclic aromatic hydrocarbon (PAH) ring formation. In particular we have determined the elementary reaction steps in the conversion of two cyclopentadienyl radicals to naphthalene. This reaction mechanism is shown to be an extension of the mechanism occurring in the H atom-assisted conversion of fulvene to benzene. The net reaction involves the formation of dihydrofulvalene, which eliminates a hydrogen atom and then rearranges to form naphthalene through a series of ring closures and openings. The importance of forming the -CR(·)-CHR-CR'=CR"- moiety, which can undergo rearrangement to form three-carbon-atom ring structures, is illustrated with the C_4H_7 system. The ability of hydrogen atoms to migrate around the cyclopentadienyl moiety is illustrated both for methyl-cyclopentadiene, $C_5H_5CH_3$, and dihydrofulvalene, $C_5H_5C_5H_5$, as well as for their radical species, C_6H_7 and $C_5H_5C_5H_4$. The mobility of hydrogen in the cyclopentadienyl moiety plays an important role both in providing resonance-stabilized radical products and in creating the -CR(·)-CHR-CR'=CR"- moiety for ring formation. The results illustrate the radical pathway for converting five-membered rings to aromatic six-membered rings. Furthermore, the results indicate the important catalytic role of H atoms in the aromatic ring formation process.

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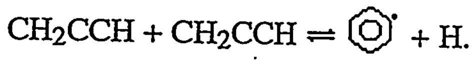
Introduction

The mechanisms of polycyclic aromatic hydrocarbon (PAH) and soot formation in flames continue to be of interest to the combustion community because of the potency of some of the PAH isomers in inducing mutations and cancer and the soot enhanced entry of the PAH's into the respiratory system. The reaction mechanism of the first aromatic ring formation in flames has been addressed by Frenklach *et al.* [1], Westmoreland *et al.* [2], Miller and Melius [3], and others [4,5]. Miller and Melius proposed a complex reaction mechanism in which two resonance-stabilized propargyl radicals, C_3H_3, combine together and rearrange to form benzene (or phenyl + H) [3],



(1)

The formation of larger polycyclic aromatic hydrocarbons (PAH's) was proposed to follow an acetylene addition mechanism [1].

Recently, we undertook comprehensive experimental and kinetic modeling studies of PAH formation in methane and ethylene flames [6]. These investigations led to the conclusions that earlier acetylene addition processes [1,2] could not account for the PAH levels observed in experimental flames. This work resulted in the need to invoke new reaction mechanisms for PAH formation. As a result of this work, we proposed that in aliphatic hydrocarbon flames the larger aromatics originate from resonance-stabilized cyclopentadienyl radicals [6]. In particular, we proposed an important new mechanism in which two cyclopentadienyl radicals, C_5H_5, combine and rearrange to form naphthalene,

(2)

The cyclopentadienyl radicals are formed from the oxidation of benzene.

We therefore have applied the quantum chemical techniques involving the BAC-MP4 [7] and BAC-MP2 [8] methods to investigate the reaction pathways and rate constants involved in the cyclopentadienyl moiety and the mechanism by which hydrocarbon ring formation occurs in unsaturated hydrocarbons. We have calculated the thermochemistry of the various tautomers and transition-state structures of C_4H_7, C_6H_7, and $C_{10}H_9$ species and have identified the important reaction pathways leading from cyclopentadienyl radical to naphthalene formation.

Theoretical Approach

The Bond-Additivity-Corrected Møller-Plessett 4th order perturbation method, BAC-MP4, has been used to determine the thermochemical properties of the intermediates and transition state structures of species including up to seven carbon atoms. Details of the method have been presented elsewhere [7]. For the larger hydrocarbons involving ten carbon atoms presented here, the BAC-MP2 method [8] has been used. The BAC-MP2 method is similar to BAC-MP4 except that 2nd order perturbation theory is used in place of 4th order. A separate set of BAC corrections, appropriate for MP2, is used for BAC-MP2. In general, the BAC-MP2 corrections are slightly smaller than the BAC-MP4 corrections. Projected MP2 energies are used to correct for spin contamination of the MP2 energies. In addition, for closed shell systems, we do not use any spin correction, even though the closed-shell UHF instability is quite large for polycyclic aromatics [9].

As an example of the accuracy of the BAC-MP2 method, in Table I we compare BAC-MP2 heats of formation with experiment for various polycyclic aromatics. On average, the BAC-MP2 method tends to underestimate the experimental values by several kJ-mol.$^{-1}$

The large differences with two of the four-ring PAH's, benzophenanthrene and naphthacene, suggest that these experimental values need re-evaluation. Considering the large degree of UHF instability in these PAH's [9], the overall accuracy is remarkably good. For radical species containing aromatics, it is more difficult to ascertain the accuracy of the BAC-MP2 method, due to uncertainties in the experimental values. However, a comparison of the BAC-MP2 and BAC-MP4 C-H bond dissociation energies (BDE's) of benzene (→ phenyl + H), 476 vs. 479 kJ-mol,$^{-1}$ indicates excellent agreement. Similarly, a comparison of the BDE's for toluene (→ benzyl + H), 369 vs. 372 kJ-mol,$^{-1}$ also indicates excellent agreement. With respect to activation energies, the ΔE for H atom addition to the ring side of fulvene, CH_2, to form $\dot{C}H_2$ is 20 kJ-mol^{-1} for the BAC-MP4 method vs. 12 kJ-mol^{-1} for the BAC-MP2 method. In general, the BAC-MP2 method gives slightly lower activation energies for radical addition to hydrocarbons. Since the BAC-MP4 activation energies seem to be slightly too high, in general, with respect to experiment, the BAC-MP2 activation energies may be in better agreement with experiment. These results thus give us some confidence in the BAC-MP2 method. The Gaussian 94 suite of quantum chemical methods [10] was used to calculate the BAC-MP2 and BAC-MP4 data. The redundant internal coordinate method [11] in Gaussian 94 was particularly helpful in solving for the transition state structures of the cyclic structures.

Ring Formation in C_4H_7

The C_4H_7 radical system is important in the formation of butadiene from vinyl radical and ethylene,

$$CH_2{=}\dot{C}H + CH_2{=}CH_2 \rightleftharpoons CH_2{=}CHCH{=}CH_2 + H. \tag{3}$$

It also represents an excellent prototype for understanding the various reaction mechanisms involved in carbon-carbon bond formation as well as for intramolecular hydrogen migration. In particular, it illustrates the ease with which the three-carbon-atom cyclic ring formation occurs. Various reaction pathways involved in the C_4H_7 system are illustrated in Fig. 1. An H atom can add to the π–bond of butadiene to form either $CH_3CHCHCH_2$ or $CH_2CH_2CHCH_2$, i.e.,

$$CH_2CHCHCH_2 + H \rightleftharpoons CH_3CHCHCH_2, \tag{4}$$

or

$$CH_2CHCHCH_2 + H \rightleftharpoons CH_2CH_2CHCH_2. \tag{5}$$

The $CH_3CHCHCH_2$ is more stable than $CH_2CH_2CHCH_2$ by 84 kJ-mol^{-1} due primarily to the resonance structure with the remaining π–bond. The barrier height for H atom addition to butadiene to form $CH_3CHCHCH_2$ is smaller than that to form $CH_2CH_2CHCH_2$, consistent with the greater exothermicity of reaction (4). The other linear species, CH_3CH_2CHCH, is less stable than $CH_2CH_2CHCH_2$ by 36 kJ-mol^{-1} due to the greater C-H bond strength of the unsaturated carbon.

With respect to ring formation, the $CH_2CH_2CHCH_2$ molecule has a special ability to form a three-membered ring [12]. The alkyl radical separated by a methylene group from a double-bonded carbon, i.e., -RC(·)-CH$_2$-CR'=CR"- is able to add to the π–bond at the nearer carbon to form a three-membered carbon ring,

$$\text{-RC}(\cdot)\text{-CH}_2\text{-CR'=CR''-} \rightleftharpoons \text{-}\overline{\mathrm{CRCH_2C}}\mathrm{R'CR''}(\cdot)\text{-}. \tag{6}$$

The reaction (6) is slightly endothermic by 6 kJ-mol,$^{-1}$ consistent with various experimental and theoretical studies (see ref. [12]). Our calculated rate constant for the reverse of reaction (6), $k_{-6} = 10^{12.95}\, exp(-33.3 / RT)$, is in excellent agreement with the experimental value [13] of $k_{-6} = 10^{13.15}\, exp(-29.5 / RT)$.

The formation of the four-membered ring from $CH_2CH_2CHCH_2$, on the other hand, takes 139 kJ-mol,$^{-1}$ comparable in energy to the C-C bond breaking to form $C_2H_3 + C_2H_4$ or to the C-H bond breaking to form C_4H_6 + H. The more stable $CH_3CHCHCH_2$ species also has a large activation energy to form its three-membered ring, somewhat greater than the C-H bond breaking to form C_4H_6 + H, reaction (4). The ease of the $-CR(\cdot)-CH_2-CR'=CR''-$ moiety to form the $-\overline{\mathrm{CRCH_2C}}\mathrm{R'CR''}(\cdot)-$ moiety is due to the easy rotation of the alkyl radical group and the vinyl group about the intermediate $-CH_2-$ group. No distortion of the vinyl group is necessary, unlike the other three- and four-membered ring formations.

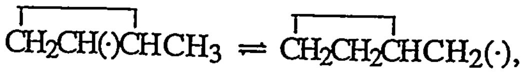
The second important illustration of the C_4H_7 system shown in Fig. 1 is the difficulty in undergoing intramolecular hydrogen migration. For instance, the 1,2-hydrogen shift,

$$\mathrm{CH_3\dot{C}HCHCH_2} \rightleftharpoons \mathrm{\dot{C}H_2CH_2CHCH_2}, \qquad (7)$$

requires an activation energy which is slightly greater than that for the hydrogen to leave and form $CH_2CHCHCH_2$, reactions (4) or (5). Even the 1,4-hydrogen shift

$$\mathrm{\dot{C}H_2CH_2CHCH_2} \rightleftharpoons \mathrm{CH_3CH_2CH\dot{C}H}, \qquad (8)$$

via a five-membered ring intermediate, has an activation energy nearly as large as the C-H or C-C bond breaking. The 1,3-hydrogen shift between the two three-membered ring compounds (not shown in Fig. 1),



$$CH_2CH(\cdot)CHCH_3 \rightleftharpoons CH_2CH_2CHCH_2(\cdot), \qquad (9)$$

has an activation energy of 164 kJ-mol^{-1} with respect to -$CH_2CH(\cdot)CHCH_3$.

Thus, it is difficult in radical species for hydrogen migration and ring formation to compete with simple bond breaking processes on a free-energy basis. Rearrangement reactions require tight transition states with loss of rotational degrees of freedom. This is particularly true for elevated temperatures (1200 - 1500K) where PAH and soot formation occur. The exception is the three-membered ring formation of reaction (6) involving the -CR($\cdot$)-CH_2-CR'=CR"- moiety, which has an extremely low activation energy that compensates for the tightness of the transition state. This important reaction mechanism has been proposed by Alder and Whittaker [14] for triene moieties leading to rearrangement of the carbon atoms in the chain and in the formation of six-membered rings from five-membered rings. As we shall see in the next sections, our calculations support these findings.

Cyclopentadienyl + Methyl Reaction

In this section we present aspects of the cyclopentadienyl moiety, C_5H_5, important in the reaction of C_5H_5 with other species. Fig. 2 shows the reaction pathway for cyclopentadienyl radical reacting with the methyl radical,

$$C_5H_5 + CH_3 \rightleftharpoons C_6H_7 + H. \qquad (10)$$

Due to the resonance stabilization of the cyclopentadienyl radical, the C_5H_5-CH_3 BDE of 5-methyl-cyclopentadiene is only 305 kJ-mol^{-1} compared with 379 kJ-mol^{-1} for the CH_3-CH_3 BDE. By moving the hydrogen atom around the cyclopentadiene ring, the methyl group can be directly bonded to one of the unsaturated carbon atoms of the ring. This gains an additional 9 kJ-mol^{-1} of stabilization energy, consistent with experimental observations [15]. More importantly, due to resonance stabilization, the resulting C-H BDE when a hydrogen atom is removed from the methyl group of 1-methyl-cyclopentadiene is only 339 kJ-mol,$^{-1}$ making reaction (10) only slightly endothermic by 25 kJ-mol.$^{-1}$

Hydrogen migration around the cyclopentadiene ring is, therefore, an important process in positioning the hydrogen atom to achieve the most stable tautomeric form. Cyclopentadiene contains the -CH=CHCH=CHCH2- moiety. The 1,5-hydrogen shift of the -CH=CHCH=CHCH2- moiety represents a concerted reaction. For the 1-5-hydrogen shift reaction of the linear molecule containing this moiety,

$$CH_2{=}CDCH{=}CHCH_3 \rightleftharpoons CH_3CD{=}CHCH{=}CH_2, \qquad (11)$$

we calculate a rate constant of $k_{11} = 10^{12.75}\, exp(-160 / RT)$, which is in excellent agreement with the experimental value [16] of $k_{11} = 10^{11.24}\, exp(-137 / RT)$ for the related reaction involving the 1,5-hydrogen shift in $CH_2{=}C(CH_3)CH{=}CHCH_3$.

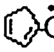
The 1,2-hydrogen migration in cyclopentadiene also corresponds to an analogous 1,5-hydrogen shift of the -CH=CHCH=CHCH2- moiety due to the ring structure. For H atom migration around cyclopentadiene, we calculate a rate constant of $k = 10^{13.63}\, exp(-128 / RT)$ in reasonable agreement with the experimental value [17] of $k = 10^{12.11}\, exp(-102 / RT)$. The BAC-MP4 method thus overestimates the activation energy for this process by ~18 kJ-mol,$^{-1}$ taking into account differences in the pre-exponential factor. For 5-methyl-cyclopentadiene, the BAC-MP4 method provides a rate constant for the 1,2-hydrogen shift of $k = 10^{13.81}\, exp(-121 / RT)$ compared with the experimental value [15] of $k = 10^{10.87}$

$exp(-83 / RT)$. In this case, the BAC-MP4 method overestimates the activation energy for this process by ~25 kJ-mol.$^{-1}$ Thus, the calculated activation energies for hydrogen migration around the cyclopentadiene ring and the methyl-substituted cyclopentadiene ring are in reasonable agreement but are slightly higher than the experimental activation energies. As discussed in the following sections, the ease with which the cyclopentadiene ring can undergo hydrogen migration is important for positioning the hydrogens to gain resonance stabilization for elimination and for further ring formation.

Hydrogen Atom Assisted Conversion of Fulvene to Benzene

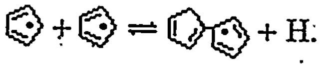
In this section we present the reaction mechanism for the conversion of fulvene to benzene catalyzed by the hydrogen atom. The reaction coordinate diagram for

 $+ H \rightleftharpoons C_5H_5CH_2 \rightleftharpoons$  $+ H$ (12)

is shown in Fig. 3. While the hydrogen atom can attack any of the π bonds to form $\dot{C}H_2$, $\dot{C}H_2$, $\dot{C}H_2$, or CH_3, the hydrogen can move around the cyclopentadiene ring, thereby connecting the first three species. Hydrogen migration is facilitated because the $\dot{C}H_2$ species contains the important -CH=CH-CHR-$CH_2(\cdot)$ moiety discussed above in the C_4H_7 section. The $\dot{C}H_2$ species can undergo cyclic ring closure with little activation energy to form the bicyclo[3.1.0] C_6H_7 species, . The resulting bicyclo[3.1.0] structure  can then undergo ring opening to form the six-membered cyclohexadienyl radical, , which can then eliminate a H atom to form benzene. It should be noted from the previous section that $\dot{C}H_2$ and $\dot{C}H_2$ (not shown in Fig. 2) are species that can be formed from the reaction of cyclopentadienyl radical with CH_3. The $\dot{C}H_2$ and $\dot{C}H_2$ species can undergo unimolecular rearrangement, as indicated in Fig. 3 to form benzene.

Conversion of Cyclopentadienyl to Naphthalene

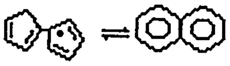
The reaction of two cyclopentadienyl radicals to form naphthalene involves two steps and involves reaction mechanisms described in each of the previous sections. The reaction coordinate diagrams for the net reaction (2) is shown in Figs. 4 and 5. The heats of formation, calculated at the BAC-MP2 level of theory, are also shown in the figures. The BDE for formation of 9,10-dihydrofulvalene, , is only 218 kJ-mol,$^{-1}$ consistent with the relatively weak bonds formed between two resonance-stabilized radicals. The two saturated carbon atoms forming the bridge between the two cyclopentadienyl moieties prevent any resonance stabilization when an H atom is removed. By shifting the H atom around the ring to form 1,10-dihydrofulvalene, , 1,5-dihydrofulvalene,, etc., an H atom can be eliminated to form, for example, , i.e.,



(13)

Reaction (13) is only slightly endothermic by 34 kJ-mol,$^{-1}$ the resulting C-H BDE of  to form the resonance-stabilized  is only 262 kJ-mol.$^{-1}$ We have not found any low-lying reaction pathway in which  can undergo carbon bond rearrangement, due to the weakness of the C-C bond. Furthermore, the resulting transition state structures for such a carbon atom rearrangement mechanism would be tight and would not be able to compete with the loose transition state structures for H atom bond scissioning.

The  radical species, on the other hand, can undergo an H atom shift on the ring to form  (see Fig. 5). This generates the -CR(·)-CHR-CR'=CR"- moiety discussed above. This can lead to the three-membered ring closure and subsequent opening of the bicyclic ring to form  (another resonance form of  is shown in Fig. 5). This species possesses another -CR(·)-CHR-CR'=CR"- moiety with respect to the other cyclopentadienyl group. This enables  to form another three-membered ring and subsequent ring opening. The resulting  radical can eliminate a H atom to form naphthalene. Thus, through a series of ring closures and openings, the cyclopentadienyl rings can be transformed to naphthalene,

 + H. (14)

Competing with this process is the elimination of the H atom from  to form fulvalene, $C_5H_4=C_5H_4$. We find that fulvalene is relatively stable to rearrangement. However, fulvalene will react with another H atom to form  or  and then rearrange to form naphthalene. This conclusion is supported by the experimental data of Alder and Whittaker [14] who suggest that the conversion of the fulvalene analog bifluorenylidene to the naphthalene analog dibenzo[g,p]chrysene requires the presence of radicals in order to undergo rearrangement, even at temperatures above 400 C. The relative stability of the dihydrofulvalene is consistent with the experimental data of Hedaya *et al.* [18]. In flash vacuum pyrolysis of nickelocene, they find 9,10-dihydrofulvalene and its various isomers are formed from cyclopentadienyl radicals. The detection of dihydrofulvalene supports our conclusion that reaction (13) is endothermic and that there are no low activation energy pathways for carbon atom rearrangement in dihydrofulvalene.

Conclusions

We have used the quantum chemical BAC-MP4 and BAC-MP2 methods to identify the reaction pathway for formation of naphthalene from two cyclopentadienyl radicals. The reaction mechanism hinges on the formation of the -CR(·)-CHR-CR'=CR"- moiety that allows the three-carbon-atom cyclic ring to be formed. The cyclopentadienyl moiety has a special ability to form the -CR(·)-CHR-CR'=CR"- structure due to the facile migration of the H atom around the five-membered ring. This concerted 1,5-hydrogen shift mechanism can occur both for closed-shell and open-shell cyclopentadienyl moieties, such as in $C_5H_5CH_3$ and in $C_5H_5\dot{C}H_2$.

These results further illustrate the important role of the cyclopentadienyl moiety in aromatic ring formation. Previously, we showed the role of fulvene (methylene-cyclopentadiene) in the reaction mechanism converting two propargyl radicals, C_3H_3, to benzene [3]. In this paper, we have shown that the hydrogen adduct of fulvene, $C_5H_5CH_2$, can also form the aromatic ring. We believe that in flames the radical pathway should be the more likely pathway for aromatic ring formation than the unimolecular rearrangement pathway. Indeed, while fulvalene, $C_5H_4C_5H_4$, is likely to be formed from hydrofulvalenyl, fulvalene needs to regain the H atom (or another radical) before the aromatic ring conversion can occur. Under sooting conditions in flames, there is likely to be a high concentration of H atoms and other radicals to allow the radical pathways, such as in Figs. 3 and 5, to proceed. The $C_5H_5CH_2$ species should also play an important role in the reaction of $C_3H_3 + C_3H_5$, i.e.,

$$C_3H_3 + C_3H_5 \rightleftharpoons C_5H_5CH_2 + H, \qquad (15)$$

followed by conversion of $C_5H_5CH_2$ to form benzene. Under flame conditions, it is possible that $C_5H_5CH_2$ will convert to fulvene + H and back as in reaction (12). These results indicate the important catalytic behavior of H atoms in the conversion of unsaturated hydrocarbons to aromatic species.

The current results further support the capability of resonance-stabilized radicals to react with each other to form aromatic rings. The resonance-stabilized cyclopentadienyl moiety will also be formed from the oxidation of larger aromatic rings (e.g., indenyl from naphthalene). The reaction of these polycyclic species with another C_5H_5 should lead to the formation of larger polycyclic aromatics [6] via a similar reaction mechanism.

References

[1] M. Frenklach, D. W. Clary, W. C. Gardiner, and S. E. Stein, Twentieth Symp. (Intern.) on Comb., p. 887, The Combustion Institute, Pittsburgh (1984); M. Frenklach and J. Warnatz, Comb. Sci. and Tech. **51**, 265 (1987).

[2] P. R. Westmoreland, A. M. Dean, J. B. Howard, and J. P. Longwell, J. Phys. Chem. **93**, 8171 (1989).

[3] J. A. Miller and C. F. Melius, Comb. Flame **91**, 21 (1992); C. F. Melius, J. A. Miller, and E. M. Evleth, Twenty-fourth Symp. (Intern.) on Comb., p. 621, The Combustion Institute, Pittsburgh (1992).

[4] R. D. Kern and K. Xie, Prog. Energy Comb. Sci. **17**, 191 (1991).

[5] S. E. Stein, J. R. Walker, M. M. Suryan, and A. Fahr, Twenty-third Symp. (Intern.) on Comb., p. 85, The Combustion Institute, Pittsburgh (1990).

[6] N. M. Marinov, W. J. Pitz, C. K. Westbrook, M. J. Castaldi, and S. M. Senkan, Comb. Sci. and Tech., submitted; M. J. Castaldi, N. M. Marinov, C. F. Melius, S. M. Senkan, W. J. Pitz, and C. K. Westbrook, Twenty-sixth Symp. (Intern.) on Comb., The Combustion Institute, Pittsburgh, submitted.

[7] C. F. Melius, in Chemistry and Physics of Energetic Materials;" NATO ASI **309**, p. 21, S. Bulusu, ed., 1990; P. Ho and C.F. Melius, J. Phys. Chem. **94**, 5120 (1990).

[8] P. Ho and C. F. Melius, J. Phys. Chem. **99**, 2166 (1995).

[9] M. E. Colvin, E. T. Seidl, C. L. Janssen, I. M. Nielsen, and C. F. Melius, submitted.

[10] Gaussian 94 (Rev B), M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. A. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Caussian Inc., Pittsburgh PA, 1995.

[11] C. Peng, P. Y. Ayala, H. B. Schlegel, and M. J. Frisch, J. Comp. Chem., submitted.

[12] A. Effio, D. Griller, K. U. Ingold, A. L. J. Beckwith, and A. K. Serelis, JACS **102**, 1734 (1980).

[13] V. W. Bowry, J. Lusztyk, and K. U. Ingold, JACS **113**, 5687 (1991); M. Newcomb and A. G. Glenn, JACS **111**, 275 (1989).

[14] R. W. Alder and G. Whittaker, J. Chem. Soc. (Perkin II) 712 (1975).

[15] S. McLean, C. J. Webster, and R. J. D. Rutherford, Can. J. Chem. **47**, 1555 (1969).

[16] H. M. Frey and R. J. Ellis, J. Chem. Soc.,4770 (1965).

[17] W. R. Roth, Tetrahedron Lett., 1009 (1964).

[18] E. Hedaya, D. W. McNeil, P. Schissel, and D. J. McAdoo, JACS **90**, 5285 (1968).

Table I. Heats of formation at 300K for various polycyclic aromatic hydrocarbons using the BAC-MP2 method and comparisons with experimental data. Energies are in kJ-mol.$^{-1}$

Species	$\Delta H^{o}_{f\,300}$ BAC-MP2	$\Delta H^{o}_{f\,300}$ Exp.[a]
1 Aromatic Ring		
benzene	84.5	82.9
toluene	51.1	50.2
ortho-xylene	17.1	19.1
meta-xylene	15.8	17.3
para-xylene	16.1	18.0
ethyl-benzene	27.1	29.9
indene	164.3	163.5
2 Aromatic Rings		
naphthalene	148.0	150.8
3 Aromatic Rings		
phenanthracene	198.6	207
anthracene	227.7	231
4 Aromatic Rings		
triphenylene	251.6	259
chrysene	256.8	263
benz[a]anthracene	270.2	
benzophenanthrene	273.0	291
naphthacene	314.7	292
5 Aromatic Rings		
benz[e]pyrene	261.4	
benz[a]pyrene	279.3	
perylene	296.9	308

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[a] J. D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, London (1970).

Figure captions

Figure 1. Reaction pathway diagram for the molecular rearrangements within the C_4H_7 system. BAC-MP4 energies (in kJ-mol^{-1}) are given for stable intermediates and transition state structures.

Figure 2. Reaction pathway diagram for the reaction of cyclopentadienyl radical with methyl radical. BAC-MP4 energies (in kJ-mol^{-1}) are given for stable intermediates and transition state structures.

Figure 3. Reaction pathway diagram for the reaction of fulvene with H atom. BAC-MP4 energies (in kJ-mol^{-1}) are given for stable intermediates and transition state structures.

Figure 4. Reaction pathway diagram for the reaction of two cyclopentadienyl radicals. BAC-MP2 energies (in kJ-mol^{-1}) are given for stable intermediates and transition state structures.

Figure 5. Reaction pathway diagram for the rearrangement of the C_5H_5-C_5H_4 radical to form naphthalene. BAC-MP2 energies (in kJ-mol^{-1}) are given for stable intermediates and transition state structures.

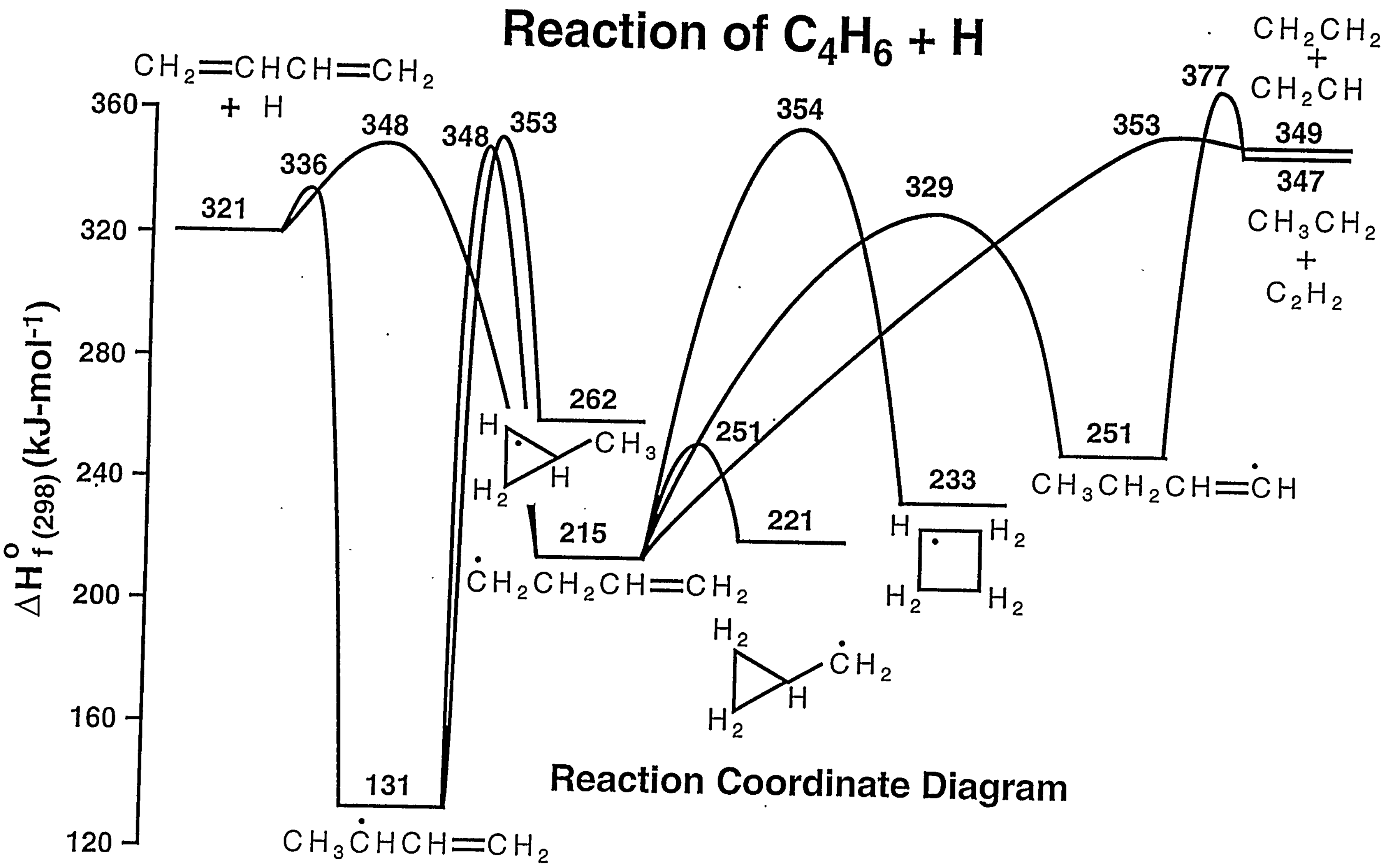

Reaction of C_4H_6 + H
$\Delta H^{o}_{f\,(298)}$ (kJ-mol^{-1})
360
320
280
240
200
160
120
$CH_2{=}CHCH{=}CH_2$ + H
321
336
348
348
353
262
CH$_3$
215
$\dot{C}H_2CH_2CH{=}CH_2$
131
$CH_3\dot{C}HCH{=}CH_2$
251
221
354
329
233
$\dot{C}H_2$
251
$CH_3CH_2CH{=}\dot{C}H$
353
377
CH_2CH_2 + CH_2CH
349
347
CH_3CH_2 + C_2H_2
Reaction Coordinate Diagram

Figure 1

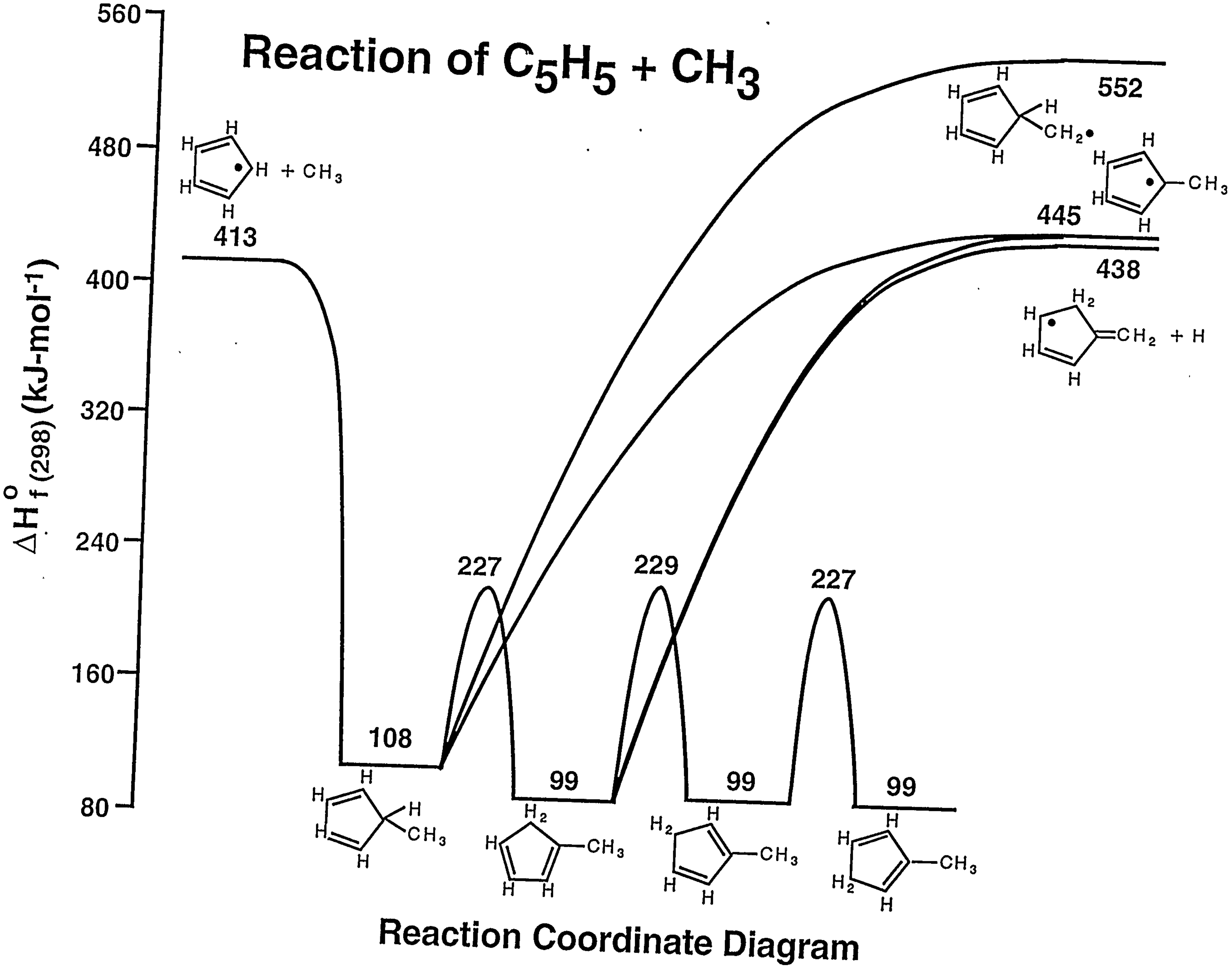

Reaction of $C_5H_5 + CH_3$
560
480
400
320
240
160
80
$\Delta H^o_{f(298)}$ (kJ-mol-1)
+ CH_3
413
108
227
99
229
99
227
99
552
445
438
CH_2•
CH_3
=CH_2 + H
Reaction Coordinate Diagram

Figure 2

Reaction of Fulvene + H

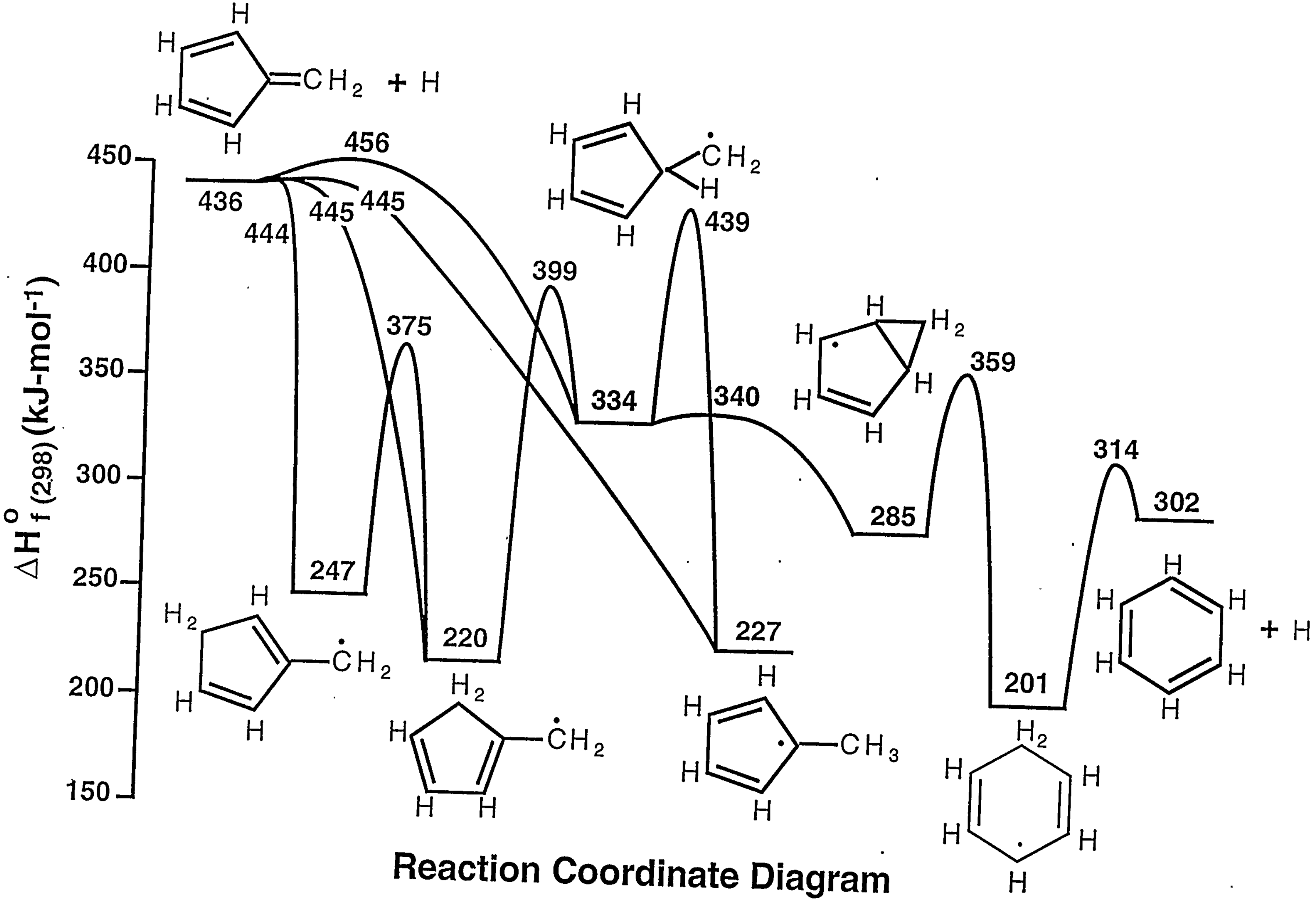


Figure 3

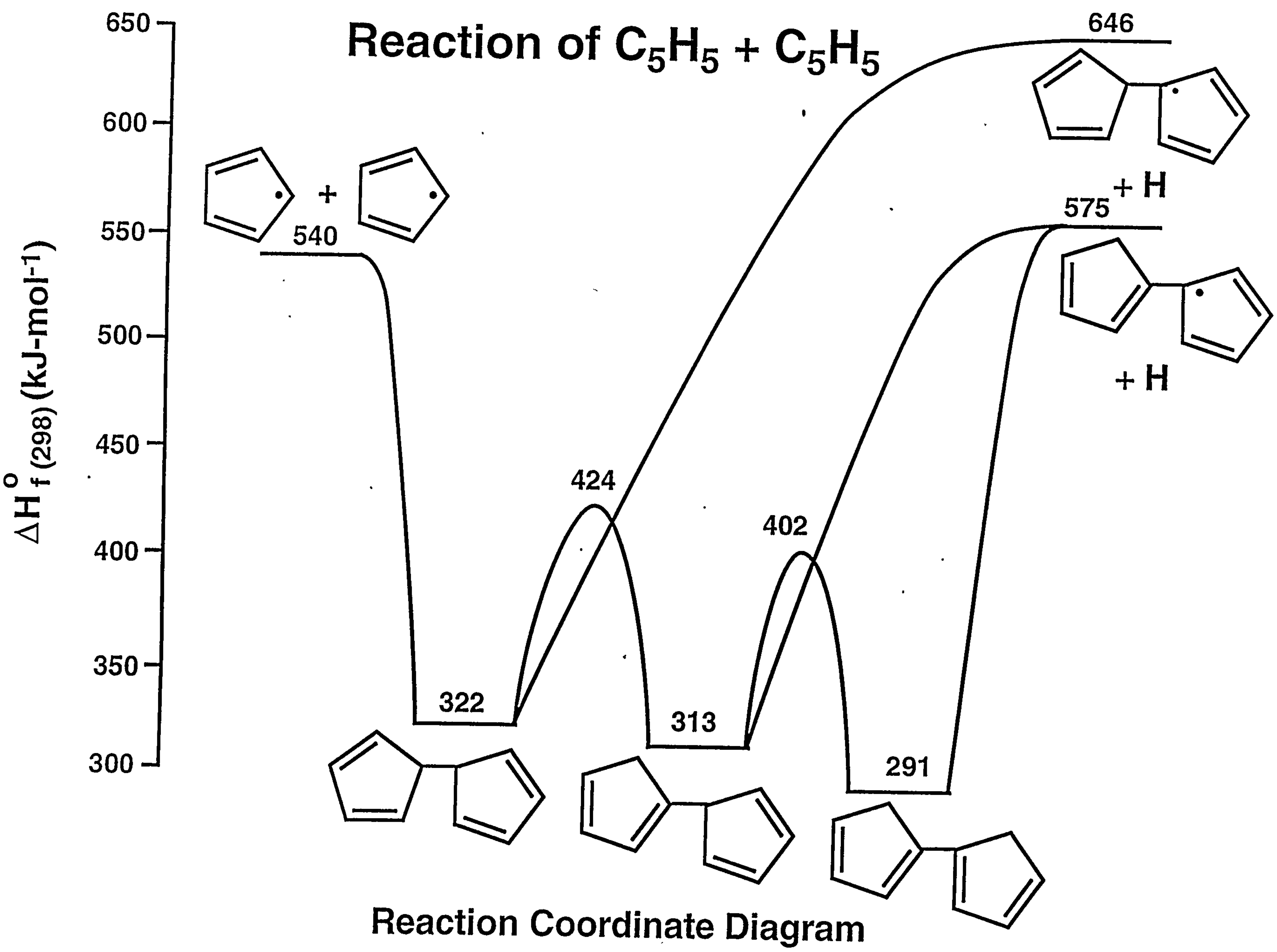
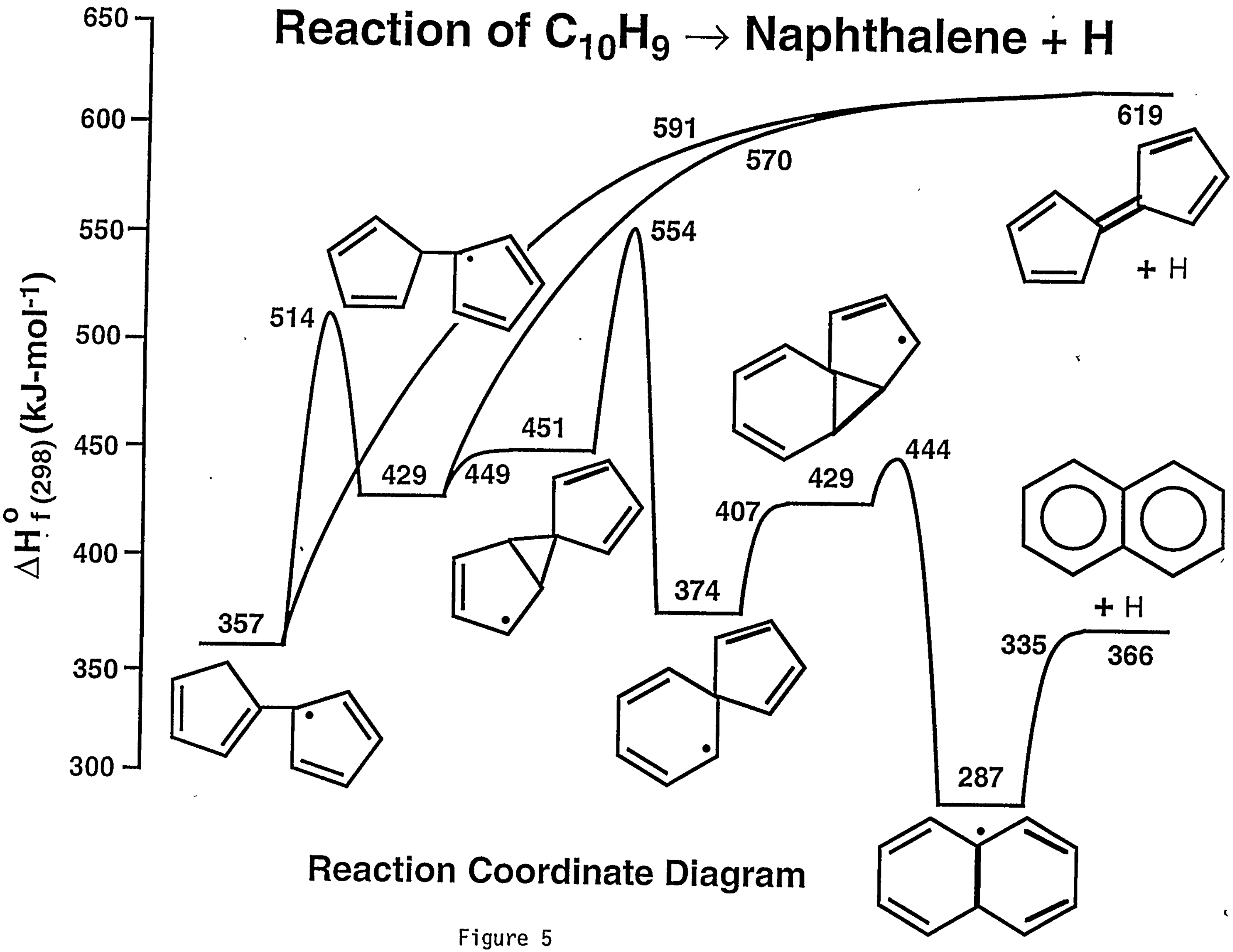

Reaction of $C_5H_5 + C_5H_5$
$\Delta H^o_{f\,(298)}$ (kJ-mol^{-1})
650
600
550
500
450
400
350
300
+
540
322
424
313
402
291
646
575
+ H
+ H
Reaction Coordinate Diagram

Figure 4

Reaction of $C_{10}H_9 \rightarrow$ Naphthalene + H



Reaction Coordinate Diagram

Figure 5