JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2001; **14:** 131–138

Thermochemistry of cyclopentadienylidene (c-C_5H_4, C_{2v}, $^3B_1$), cyclopentadienyl radical (c-$C_5H_5^\bullet$, C_{2v}, $^2B_1$) and 1,3-cyclopentadiene (c-C_5H_6, C_{2v}, $^1A_1$): a theoretical study by the G2M(RCC,MP2) method

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Received 7 July 2000; revised 9 November 2000; accepted 13 November 2000

ABSTRACT: The thermochemistry of c-C_5H_4 ($^3B_1$), c-$C_5H_5^\bullet$ and c-C_5H_6 was investigated at the G2M(RCC,MP2) level. The heat of formation ($\Delta H^o_{f,298}$), ionization potential (*IP*), electron affinity (*EA*) and proton affinity (*PA*) are respectively, 125.1, 204.4, 42.5 and 230.7 kcal mol^{-1} for c-C_5H_4 ($^3B_1$), 63.5, 195.2, 44.9 and 197.2 kcal mol^{-1} for c-$C_5H_5^\bullet$ and 32.1, 199.9, 26.0 and 195.2 kcal mol^{-1} for c-C_5H_6. The computed values for the last two molecules are in excellent agreement with available experimental data, with the errors of ± 1 and ± 2 kcal mol^{-1} for the heat of formation and the other parameters, respectively. In addition, the heat of formation of c-$C_5H_4^{\bullet-}$ is evaluated as 82.0 kcal mol^{-1}, about 10 kcal mol^{-1} higher than the experimental value. This leads to the suggestion that the experimental $\Delta H^o_{f,298}$(c-$C_5H_4^{\bullet-}$) value needs to be re-examined. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: *ab initio* calculations; G2M method; thermochemistry; cyclopentadienyl radical; cyclopentadienylidene; 1,3-cyclopentadiene

INTRODUCTION

As important intermediate species in oxidation reactions of benzene and toluene at high temperature, three cyclopentadiene hydrocarbons, cyclopentadienylidene (c-C_5H_4), the cyclopentadienyl radical (c-$C_5H_5^\bullet$) and 1,3-cyclopentadiene (c-C_5H_6), have been the subjects of numerous experimental and theoretical studies.[1–7] While the cyclopentadienyl radical is an important ligand in many inorganic complexes, cyclopentadienylidene, the second organic ring (the first one is c-C_3H_2), is assumed to exist in interstellar space.[2]

The lowest energy geometric configurations of c-C_5H_6, c-$C_5H_5^\bullet$ and c-C_5H_4 have C_{2v} symmetry and their ground electronic states are $^1A_1$, $^2B_1$ and $^3B_1$, respectively. These facts are well established by both theoretical calculations and experiment.

The thermochemical parameters of c-C_5H_6 and c-$C_5H_5^\bullet$, including the heat of formation ($\Delta H^o_{f,298}$), ionization potential (*IP*), electron affinity (*EA*) and proton affinity (*PA*), are well known, but the thermochemical parameters of c-C_5H_4 remain controversial. A large discrepancy between the reported experimental and theoretical results for the heat of formation of c-C_5H_4 ($^3B_1$) exists. In early theoretical studies, Glukhovtsev *et al.*[3] and later Bolfill *et al.*[1] reported $\Delta H^o_{f,298}$(c-C_5H_4) as 119.4 and 119.5 kcal mol^{-1}, respectively (1 kcal = 4.184 kJ). These values were based on semi-empirical calculations at the MNDO level. In a more recent computational study, Wang and Brezinsky,[5] using a higher theoretical level, the G2(MP2,SVP) and G2(B3LYP/MP2,SVP) methods and Eqn. (1), arrived at a value of 125.2 kcal mol^{-1}. The reported value of 125.2 kcal mol^{-1} is similar to those in Refs 1 and 3 (a difference of ca. 5.5 kcal mol^{-1}) but varies greatly from the experimentally obtained value of 112.3 ± 4.7 kcal mol^{-1}.[4]

$$c-C_5H_4(^3B_1) + 6CH_4 \rightarrow: CH_2(^3B_1) + 3C_2H_6 + 2C_2H_4 \quad (1)$$

These differences might be attributed to either the accuracy of the level of theory used or the experimental heat of formation of c-$C_5H_4^{\bullet-}$ of 71.9 ± 3.6 kcal mol^{-1} chosen as the reference by McDonald *et al.*[4] is uncertain. $\Delta H^o_{f,298}$(c-$C_5H_4^{\bullet-}$) was derived from *PA*(c-$C_5H_4^{\bullet-}$) =

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Contract/grant sponsor: Academia Sinica.
Contract/grant sponsor: National Science Council of ROC; *Contract/grant number:* NSC 8902113-M-001-069.

378.2 ± 2.4 kcal mol^{-1}, $\Delta H^{o}_{f,298}$(c-$C_5H_5^{\bullet}$) = 60.9 ± 1.2 kcal mol^{-1} and $\Delta H^{o}_{f,298}(H^+)$ = 367.2 kcal mol^{-1}.

Considering the large discrepancy and importance of accurate data for these reference species, in this study we set out to re-examine the thermochemical parameters for cyclopentadienylidene (c-C_5H_4), cyclopentadienyl radical (c-$C_5H_5^{\bullet}$) and 1,3-cyclopentadiene (c-C_5H_6) using our G2M(RCC,MP2) method. The calculated parameters for c-$C_5H_5^{\bullet}$ and c-C_5H_6 were compared with available experimental results in order to check the accuracy of our theoretical method. The heat of formation of c-$C_5H_4^{\bullet-}$ was also re-computed, based on five different working reactions. Finally, dissociation energies for the C—H bond in the title species were also investigated.

COMPUTATIONAL METHODS

All calculations were performed using the G2M(RCC,MP2) method,[8] a variant of the G2 method.[9] This method gives an approximation to the RCCSD(T)/6–311+G(3df,2p) energies and includes the empirical 'higher level correction' also used in G2.[9] It uses B3LYP/6–311G(d,p) optimized geometries and ZPE corrections (thermal corrections in this paper) and substitutes the QCISD(T)/6–311G(d,p) calculation of the original G2 scheme by the restricted coupled cluster[10] RCCSD(T)/6–311G(d,p) calculation. It should be mentioned that the G2M method can be also applied using MP2/6–31G* geometries and frequencies,[8] but the accuracy expected in this case is similar or slightly worse than with B3LYP geometries. The total energy in G2M(RCC,MP2) is computed as follows:

$$\begin{aligned} E[\mathrm{G2M(RCC,MP2)}] = {} & E[\mathrm{MP2/6-311+G(3df,2p)}] \\ & + E[\mathrm{RCCSD(T)/6-311G(d,p)}] \\ & - E[\mathrm{MP2/6-311G(d,p)}] \\ & + \Delta E(\mathrm{HLC}) \\ & + \mathrm{TC[B3LYP/6-311G(d,p)]} \end{aligned} \quad (2)$$

with the 'higher level correction,'

$$\Delta E(\mathrm{HLC}) = -5.25n_\beta - 0.19n_\alpha \quad (3)$$

where n_α and n_β are the numbers of α and β valence electrons, respectively. It is known that the expected accuracy of this computational scheme is within 1–2 kcal mol^{-1}.[8,9] When necessary, the Gaussian-3 (G3) theory which is based on MP2/6–31G* optimized geometries[11] and the CCSD(T)/6–311+G(3df,2p) level were also used to test the accuracy of our calculations. The Gaussian 98[12] and *ab initio* MOLPRO 98[13] programs were employed for the calculations.

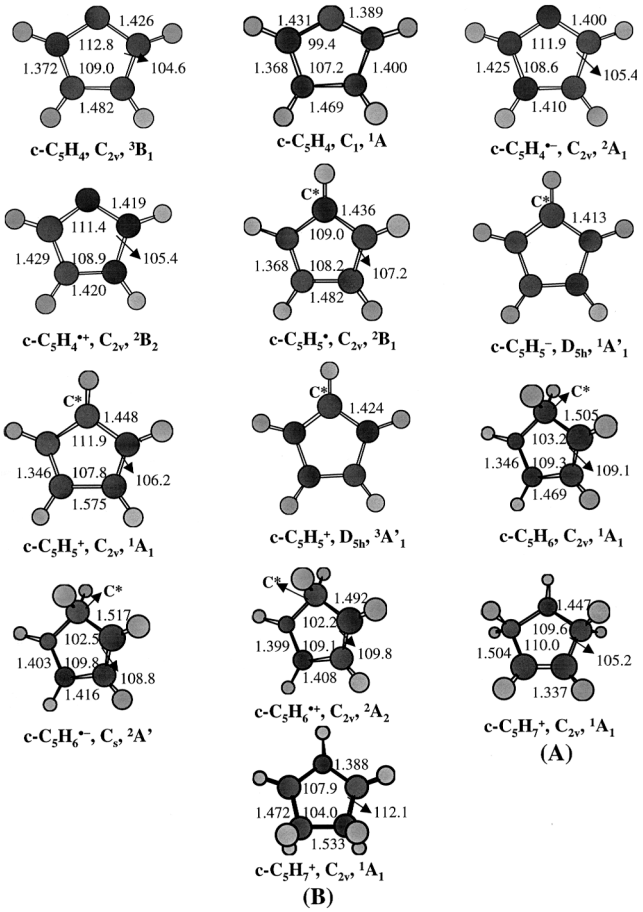

Figure 1. B3LYP/6–311G(d,p) optimized geometries of various cyclopentadiene hydrocarbons. Bond lengths are in Å and bond angles in degrees

RESULTS AND DISCUSSION

Optimized geometries of various species are shown in Fig. 1. Calculated total energies and experimental heats of formation of the reference species are presented in Table 1. Table 2 summarizes the heats of formation of c-C_5H_4 ($^3B_1$), c-$C_5H_5^{\bullet}$, c-C_5H_6 and c-$C_5H_4^{\bullet-}$ calculated by employing ten, three, six and five different working reactions, respectively. Table 3 summarizes other thermochemical parameters of c-C_5H_4 ($^3B_1$), c-$C_5H_5^{\bullet}$ and c-C_5H_6 such as *IP*, *EA* and *PA*. Where possible, computed values are compared with available experimental data. Table 4 shows the results for heats of formation of c-$C_5H_4^{\bullet+}$, c-$C_5H_5^+$ ($^1A_1$), c-$C_5H_5^+$ ($^3A_1'$), c-$C_5H_5^-$, c- $C_5H_6^{\bullet+}$ and c-$C_5H_6^{\bullet-}$. The calculated result for c-$C_5H_5^-$ is used for comparison with the experimental value in order to have a further check of the accuracy of our method. Finally, Table 5 summarizes the dissociation energies of C-H bonds in c-$C_5H_5^+$ ($^1A_1$), c-$C_5H_5^+$ ($^3A_1'$), c-$C_5H_5^-$, c-C_5H_6, c-$C_5H_6^{\bullet+}$ and c-$C_5H_6^{\bullet-}$.

As seen in Table 2, the values for the heat of formation

Table 1. Calculated total energies (in hartrees), thermal corrections (in kcal mol^{-1}) and experimental heats of formation (in kcal mol^{-1}) of various C_nH_n species

Species	MP2/6–311G(d,p)	CCSD(T)/ 6–311G(d,p)	MP2/ 6–311+G(3df,2p)	TC[a]	G2M (RCC,MP2)	$\Delta H^o_{f,298}$[b]
H^+	0	0	0	0	0	365.7[c]
$H^\bullet$	−0.49981	−0.49981	−0.49981	0.0	−0.50000	52.10
H_2	−1.16025	−1.16834	−1.16273	7.80	−1.16383	0.00
$:CH_2$ ($^1A_1$)	−39.00441	−39.03472	−39.02810	12.12	−39.05542	102.7[d]
$:CH_2$ ($^3B_1$)	−39.03306	−39.05464	−39.05229	12.57	−39.06510	93.8[d]
$^{-\bullet}CH_2$	−39.01215	−39.03653	−39.06564	11.00	−39.08900	78.3 ± 2.0
$^\bullet CH_3$	−39.70724	−39.73223	−39.73133	20.48	−39.74019	34.82
$^+CH_3$	−39.35618	−39.38112	−39.37505	21.35	−39.38229	261.71
$^-CH_3$	−39.67027	−39.69498	−39.72702	19.18	−39.74292	33.10 ± 0.9
CH_4	−40.37923	−40.40583	−40.40564	29.78	−40.40654	−17.89
C_2H_2	−77.11071	−77.13879	−77.15662	18.70	−77.18210	54.19
C_2H_4	−78.34416	−78.38371	−78.39332	33.79	−78.41166	12.54
$C_2H_5^-$	−78.86356	−78.90640	−78.93809	37.63	−78.95904	34.3 ± 2.1
C_2H_6	−79.57087	−79.61568	−79.62018	48.86	−79.62521	−20.04
$H_3C—C\equiv CH$	−116.31358	−116.35866	−116.38457	37.30	−116.41373	44.32
c-C_3H_4	−116.27582	−116.32172	−116.34677	37.10	−116.37707	66.2[e]
$H_2C=CHCH_3$	−117.54350	−117.60019	−117.61677	52.35	−117.63899	4.88
c-C_3H_6	−117.53652	−117.58926	−117.60887	52.93	−117.62622	12.74
C_3H_8	−118.76598	−118.82858	−118.83892	67.48	−118.84838	−25.02
$H_2C=CH—CH=CH_2$	−155.52226	−155.59031	−155.61933	56.12	−155.65779	26.00
c-C_5H_4 (D_{2d}, $^1A_1$)	−192.17037	−192.23418	−192.28730	43.11	−192.34769	150.5 ± 2[f]
c-C_5H_4(C_{2v}, $^3B_1$)	−192.20308	−192.28665	−192.31664	44.41	−192.38966	
c-C_5H_4 (C_1, ^1A)	−192.20219	−192.27187	−192.31942	44.26	−192.38385	
c-$C_5H_4^{\bullet-}$ (C_{2v}, $^2A_1$)	−192.26286	−192.32629	−192.39804	43.48	−192.45765	
c-$C_5H_4^{\bullet+}$ (C_{2v}, $^2B_2$)	−191.88578	−191.96903	−191.99087	44.14	−192.06381	
c-$C_5H_5^\bullet$ (C_{2v}, $^2B_1$)	−192.88364	−192.96786	−193.00129	51.73	−193.06854	63.6 ± 1.0[g]
c-$C_5H_5^+$ (C_{2v}, $^1A_1$)	−192.58586	−192.66094	−192.69669	52.60	−192.75323	
c-$C_5H_5^+$ (D_{5h}, $^3A_1'$)	−192.60328	−192.67204	−192.71287	53.05	−192.75731	
c-$C_5H_5^-$ (D_{5h}, $^1A_1'$)	−192.95218	−193.01279	−193.09086	51.39	−193.14029	
c-C_5H_6 (C_{2v}, $^1A_1$)	−193.53597	−193.60871	−193.65441	60.44	−193.70155	32.1 ± 0.4[e]
c-$C_5H_6^{\bullet+}$ (C_{2v}, $^2A_2$)	−193.22252	−193.30279	−193.33332	60.40	−193.38281	
c-$C_5H_6^{\bullet-}$ (C_s, ^2A)	−193.46148	−193.53881	−193.60175	56.26	−193.66033	
c-$C_5H_6^{\bullet-}$ (C_{2v}, $^2B_1$)	−193.46129	−193.53855	−193.60149	55.57	−193.66110	
c-$C_5H_7^+$ (C_{2v}, $^1A_1$) *A*	−193.81554	−193.89699	−193.92888	65.80	−193.97619	
c-$C_5H_7^+$ (C_{2v}, $^1A_1$) *B*	−193.85922	−193.93735	−193.97194	67.88	−194.01262	

[a]Including zero-point energy and thermal correction at 298 K using unscaled frequencies.
[b]Experimental values are taken from Ref. 16, unless mentioned otherwise.
[c]Derived from the $H^+ + e^- \rightarrow H^\bullet$ reaction and $\Delta H^o_{f,298}(H^\bullet)_{exp}$ = 52.10 kcal mol^{-1} from Ref. 16.
[d]Experimental value from Ref. 17.
[e]Experimental value from Ref. 18.
[f]Theoretical value from Ref. 14.
[g]Experimental value from Ref. 19.

of c-C_5H_4 ($^3B_1$) computed by using 10 different working reactions (4)–(13) are internally consistent; with an error bar of ca. 0.9 kcal mol^{-1}. The smallest and largest values are obtained from reactions (5) and (7), respectively. Reaction (5) is an isomerization and the result is based upon the heat of formation of spiropentadiene (c-C_5H_4), calculated in our previous paper,[14] 150.5 ± 2 kcal mol^{-1}. This value was also obtained from 27 different working reactions at the G2M(RCC,MP2) level. Thus, similar error bars of ±2 kcal mol^{-1} can be expected for $\Delta H_f^o{}_{,298}$ of c-C_5H_4 ($^3B_1$) obtained from reaction (5). Reaction (7) is not isodesmic. Although two C=C double bonds are conserved, a cycle and a lone-pair are changed into a C≡C triple bond. This can explain why the largest value is obtained. Reaction (4) was used by Wang and Brezinsky.[5] An interesting point comes from reaction (4) from which a value of 125.4 kcal mol^{-1} is derived. This is in good agreement with reported value of 125.2 kcal mol^{-1} (see Ref. 5) derived at the G2(B3LYP,MP2,SVP) level. Taking the average of the computed values as our best estimate, the standard heat of formation of c-C_5H_4 ($^3B_1$) can thus be proposed as 125.1 kcal mol^{-1}, with a probable error of ±1 kcal mol^{-1}. This value is in excellent agreement with that of Wang and Brezinsky,[5] but still differs from the experimentally determined value.[4] As mentioned above, these

Table 2. Calculated heats of formation (in kcal mol^{-1}) for cyclopentadienylidene (c-C_5H_4, C_{2v}, $^3B_1$), 1,3-cyclopentadiene (c-C_5H_6, C_{2v}, $^1A_1$), cyclopentadienyl radical (c-$C_5H_5^{\bullet}$, C_{2v}, $^2B_1$) and cyclopentadienylidene radical anion (c-$C_5H_4^{\bullet-}$, C_{2v}, $^2A_1$) from energies ($\Delta H_{r,298}$ in kcal mol^{-1}) of different working reactions by the G2M(RCC,MP2) method

Reaction No.	Reaction	$\Delta H^o_{r,298}$	$\Delta H^o_{f,298}$	$\Delta H^o_{f,298\ exp.}$
(4)	c-C_5H_4 ($^3B_1$) + $6CH_4$ → :CH_2 ($^3B_1$) + $3C_2H_6$ + $2C_2H_4$	40.71	125.4	
(5)	c-C_5H_4 ($^3B_1$) → c-C_5H_4 (Spiropentadiene)[a]	26.34	124.2	
(6)	c-C_5H_4 ($^3B_1$) + CH_4 → C_4H_6(1,3-but.) + C_2H_2	−27.41	125.5	
(7)	c-C_5H_4 ($^3B_1$) + C_2H_6 → C_4H_6 (1,3-but.) + HC≡C-CH_3	−35.55	125.9	
(8)	c-C_5H_4 ($^3B_1$)+ C_3H_8 → $2C_4H_6$ (1,3-but.)	−48.65	125.7	
(9)	c-C_5H_4 ($^3B_1$) + C_2H_6 → C_4H_6 (1,3-but.) + :CH_2($^3B_1$) + C_2H_2	68.95	125.1	
(10)	c-C_5H_4 ($^3B_1$) + C_3H_8 → C_4H_6 (1,3-but.) + :CH_2($^3B_1$) + HC≡C—CH_3	63.65	125.5	
(11)	c-C_5H_4 ($^3B_1$) + C_3H_8 → C_4H_6 (1,3-but.) + :CH_2($^3B_1$) + c-C_3H_4	86.65	124.4	
(12)	c-C_5H_4 ($^3B_1$) + C_3H_8 + H_2 → C_4H_6 (1,3-but.) + :CH_2($^3B_1$) + c-C_3H_6	33.11	124.5	
(13)	c-C_5H_4 ($^3B_1$) + C_3H_8 + H_2 → C_4H_6 (1,3-but.) + :CH_2($^3B_1$) + n−C_3H_6	25.10	124.6	
	Average = $1/N\Sigma(\Delta H^o_{f,298})_i$ with $N = 10$		**125.1**	
	Error = [Max($\Delta H^o_{f,298}$) − Min($\Delta H^o_{f,298}$)]/2		0.9	
(14)	c-C_5H_6 + CH_4 → C_4H_6 (1,3-but.) + C_2H_4	24.25	32.2	
(15)	c-C_5H_6 + C_2H_6 → C_4H_6 (1,3-but.) + c-C_3H_6	26.83	32.0	32.1 ± 0.4[c]
(16)	c-C_5H_6 + C_2H_6 → C_4H_6 (1,3-but.) + n-C_3H_6	18.81	32.1	31.89[d]
	Average = $1/N\Sigma(\Delta H^o_{f,298})_i$ with $N = 3$		**32.1**	33.2[e]
	Error = [Max($\Delta H^o_{f,298}$) − Min($\Delta H^o_{f,298}$)]/2		0.1	
(17)	c-$C_5H_5^{\bullet}$ + CH_4 → c-C_5H_6 [b] + $^{\bullet}CH_3$	20.92	63.9	
(18)	c-$C_5H_5^{\bullet}$ + $H^{\bullet}$ → c-C_5H_6 [b]	−83.46	63.4	
(19)	c-$C_5H_5^{\bullet}$ + C_2H_6 → C_4H_6 (1,3-but.) + $^{\bullet}CH_3$ + C_2H_2	71.33	63.7	60.9 ± 1.2[f]
(20)	c-$C_5H_5^{\bullet}$ + C_2H_6 + H_2 → C_4H_6 (1,3-but.) + $^{\bullet}CH_3$ + C_2H_4	30.08	63.3	63 ± 2[g]
(21)	c-$C_5H_5^{\bullet}$ + C_3H_8 + H_2 → C_4H_6 (1,3-but.) + $^{\bullet}CH_3$ + n-C_3H_6	27.47	63.3	63.2[h]
(22)	c-$C_5H_5^{\bullet}$ + C_3H_8 + H_2 → C_4H_6 (1,3-but.) + $^{\bullet}CH_3$ + c-C_3H_6	35.49	63.1	63.6 ± 1.0[f]
	Average = $1/N\Sigma(\Delta H^o_{f,298})_i$ with $N = 6$		**63.5**	
	Error = [Max($\Delta H^o_{f,298}$) − Min($\Delta H^o_{f,298}$)]/2		0.4	
(23)	c-$C_5H_4^{\bullet-}$ + CH_4 → c-C_5H_6 [b] + $CH_2^{\bullet-}$	46.21	82.1	
(24)	c-$C_5H_4^{\bullet-}$ + CH_4 → c-$C_5H_5^{\bullet}$ [b] + CH_3^-	33.09	81.4	
(25)	c-$C_5H_4^{\bullet-}$ + C_2H_6 − c-$C_5H_5^{\bullet}$ + $C_2H_5^-$	34.68	83.1	
(26)	c-$C_5H_4^{\bullet}$ − e^- → c-C_5H_4 ($^3B_1$)[b]	42.54	82.5	
(27)	c-$C_5H_4^{\bullet-}$ + H^+ → c-$C_5H_5^{\bullet}$	−383.35	81.1	
	Average = $1/N\Sigma(\Delta H^o_{f,298})_i$ with $N = 5$		**82.0**	
	Error = [Max($\Delta H^o_{f,298}$) − Min($\Delta H^o_{f,298}$)]/2		1.0	

[a] $\Delta H^o_{f,298}$(spiropentadiene) = 150.5 ± 2 kcal mol^{-1} from Ref. 14.
[b] Heats of formation of c-C_5H_4 ($^3B_1$), c-$C_5H_5^{\bullet}$ and c-C_5H_6 are 125.1, 63.5 and 32.1 kcal mol^{-1}, respectively, taken from the previous calculations.
[c] From Ref. 18.
[d] From Ref. 20.
[e] From Ref. 21.
[f] From Ref. 19.
[g] From Ref. 22.
[h] From Ref. 23.

discrepancies can be due to the use of insufficiently accurate theoretical level or the uncertainty of the $\Delta H^o_{f,298}$(c-$C_5H_4^{\bullet-}$) value of 71.9 ± 3.6 kcal mol^{-1}.

In order to test the accuracy of our method, the heat of formation of c-C_5H_4 ($^3B_1$) was also calculated using the G3 and CCSD(T)/6–311+G(3df,2p) methods. Based upon the computed atomization energy, a value of 124.6 kcal mol^{-1} for the heat of formation of c-C_5H_4 ($^3B_1$) was derived using the G3 method. Another value of 124.8 kcal mol^{-1} was computed at the CCSD(T)/6–311+G(3df,2p) level based on the working reaction (4). These values agree well with 125.1±1 kcal mol^{-1} obtained at the G2M level.

We also tested our method by calculations of heats of formation of similar molecules and comparison of obtained values with available experimental data. 1,3-Cyclopentadiene (c-C_5H_6) and cyclopentadienyl radical (c-$C_5H_5^{\bullet}$) were chosen as the best examples because they have geometries similar to that of c-C_5H_4 and their available experimental data are well established. The heats of formation of c-C_5H_6 and c-$C_5H_5^{\bullet}$ were computed by using three and six different working reactions (14)–(16) and (17)–(22), respectively (see Table 2). The calculated values are internally consistent, with errors of only 0.1 and 0.4 kcal mol^{-1}. Our best values taken as the average of computed values are 32.1 and 63.5 kcal mol^{-1}. Heats of formation for c-C_5H_6 and c-$C_5H_5^{\bullet}$ were also calculated using the G3 method and the values of 32.7 and 63.9 kcal mol^{-1}, respectively, were obtained. The results are in excellent agreement with all available

Table 3. Calculated ionization potentials (*IP* in kcal mol^{-1}), electron affinities (*EA* in kcal mol^{-1}) and proton affinities (*PA* in kcal mol^{-1}) for cyclopentadienylidene (c-C_5H_4, C_{2v}, $^3B_1$), cyclopentadienyl radical (c-$C_5H_5^{\bullet}$, C_{2v}, $^2B_1$) and 1,3-cyclopentadiene (c-C_5H_6, C_{2v}, $^1A_1$)

Species	Parameter	Reaction No.	Reaction	Calculated result	Experimental data
c-C_5H_4 (C_{2v}, $^3B_1$)	*IP*	(28)	c-$C_5H_4 \rightarrow$ c-$C_5H_4^{\bullet+} + e^-$	204.4	
	EA	(29)	c-$C_5H_4^{\bullet-} \rightarrow$ c-$C_5H_4 + e$	42.5	
	PA	(30)	c-$C_5H_5^+$ ($^1A_1$) $\rightarrow$ c-$C_5H_4 + H^+$	228.1	
		(31)	c-$C_5H_5^+$ ($^3A_1'$) $\rightarrow$ c-$C_5H_4 + H^+$	230.7	
c-$C_5H_5^{\bullet}$ (C_{2v}, $^2B_1$)	*IP*	(32)	c-$C_5H_5^{\bullet} \rightarrow$ c-$C_5H_5^+$ ($^1A_1$) $+ e^-$	197.7	197.39[a]
		(33)	c-$C_5H_5^{\bullet} \rightarrow$ c-$C_5H_5^+$ ($^3A_1'$) $+ e$	195.2	193.93[b]
					200.39 ± 2.31[c]
	EA	(34)	c-$C_5H_5^- \rightarrow$ c-$C_5H_5^{\bullet} + e$	44.9	40.82 ± 2.54[d]
					41.19 ± 0.46[e]
					41.25 ± 1.08[f]
					42.41 ± 0.69[g]
					$<50.73 \pm 6.92$[h]
	PA	(35)	c-$C_5H_6^{\bullet+} \rightarrow$ c-$C_5H_5^{\bullet} + H^+$	197.2	198.7[k]
					194.63[l]
c-C_5H_6 (C_{2v}, $^1A_1$)	*IP*	(36)	c-$C_5H_6 \rightarrow$ c-$C_5H_6^{\bullet+} + e^-$	199.9	197.62 ± 0.23[m]
					197.85 ± 0.23[n]
					207.54[o]
	EA	(37)	c-$C_5H_6^{\bullet-} \rightarrow$ c-$C_5H_6 + e^-$	26.0	
	PA	(38)	c-$C_5H_7^+$(A) $\rightarrow$ c-$C_5H_6 + H^+$	172.3	
		(39)	c-$C_5H_7^+$(B) $\rightarrow$ c-$C_5H_6 + H^+$	195.2	196.4[k]

[a]From Ref. 24.
[b]From Ref. 25.
[c]From Ref. 26.
[d]From Ref. 27.
[e]From Ref. 28.
[f]From Ref. 4.
[g]From Ref. 29.
[h]From Ref. 30.
[k]From Ref. 31.
[l]From Ref. 32.
[m]From Ref. 33.
[n]From Ref. 34.
[o]From Ref. 35.

experimental data from Refs. 18–23. The discrepancies between calculated and experimental values are <0.5 kcal mol^{-1}, which lies within the error range of the experimental data.

In order to check our supposition further, we reinvestigated the $\Delta H^{o}_{f,298}$(c-$C_5H_4^{\bullet-}$) value of 71.9 ± 3.6 kcal mol^{-1}. Recently, $\Delta H^{o}_{f,298}$(c-$C_5H_4^{\bullet-}$) was estimated as 83 kcal mol^{-1} by Wang and Brezinsky,[5] based on the atomization energy at the G2(B3LYP,MP2,SVP) level. This value looks reasonable since based on it, $\Delta H^{o}_{f,298}$ of c-C_5H_4 ($^3B_1$) can be obtained as 125 kcal mol^{-1}. However, the result derived from atomization energy might not be accurate. Therefore, we recalculated the heat of formation of c-$C_5H_4^{\bullet-}$ employing five different working reactions (see Table 2). The values obtained are internally consistent, with an approximate error of 1 kcal mol^{-1}. The largest value is derived from the isodesmic reaction (25) and the reference $\Delta H^{o}_{f,298}$($C_2H_5^-$) value[16] of 34.3 kcal mol^{-1} with a fairly large possible error of ± 2.1 kcal mol^{-1}. The smallest value is obtained from the *PA* of c-$C_5H_4^{\bullet-}$ [reaction (27)], which was used by McDonald *et al.*[4] The *PA*(c-$C_5H_4^{\bullet-}$) value of 383.4 kcal mol^{-1} computed by us at the G2M(RCC,MP2) level is about 5 kcal mol^{-1} higher than that reported by McDonald *et al.*,[4] 378.2 ± 2.4 kcal mol^{-1}. In order to check *PA*(c-$C_5H_4^{\bullet-}$) further, we used several higher theoretical levels such as CCSD(T)/6–311+G(3df,2p), CCSD(T)/6–311++G(3df,2p) and CCSD(T)/aug-cc-pVTZ and obtained the values of 383.5, 383.6 and 383.9 kcal mol^{-1}, respectively. These results are consistent and agree with the G2M(RCC,MP2) value within 0.6 kcal mol^{-1}, i.e., within the expected error range of the G2M(RCC,MP2) method, ± 2 kcal mol^{-1}. Taking the average of the five calculated values as our best estimate, the standard heat of formation of c-$C_5H_4^{\bullet-}$ can thus be proposed as 82.0 kcal mol^{-1}, with a possible error of ± 1.5 kcal mol^{-1}. This value is about 10 kcal mol^{-1} higher than that used by McDonald *et al.*[4] The disagreement between the calculated and experimental values of 10 kcal mol^{-1} leads to the suggestion that these experimental data needs to be re-examined.

Next, it was also of interest to compute the other thermochemical parameters, *IP*, *EA* and *PA*, of c-C_5H_4

Table 4. Table 4. Calculated heats of formation (in kcal mol^{-1}) for c-$C_5H_4^{\bullet}$, c-$C_5H_5^+$ ($^1A_1$), c-$C_5H_5^+$ ($^3A_1'$), c-$C_5H_5^-$, c-$C_5H_6^{\bullet}$ and c-$C_5H_6^{\bullet}$

Species	Reaction No.	Reaction	Enthalpy of reaction	Calculated result	Experimental data
c-$C_5H_4^{\bullet+}$ (C_{2v}, $^2B_2$)	(40)	c-$C_5H_4^{\bullet+}$ + CH_4 → c-$C_5H_5^{\bullet}$ + CH_3^+	12.25	330.8	
	(41)	c-$C_5H_4^{\bullet+}$ + H_2 → c-$C_5H_5^{\bullet}$ + H^+	99.83	329.4	
	(42)	c-$C_5H_4^{\bullet+}$ + e^- → c-C_5H_4($^3B_1$)	−204.35	329.4	
		Average = $(1/N)\Sigma(\Delta H^o_{f,298})_i$ with $N = 3$		329.9	
c-$C_5H_5^+$ (C_{2v}, $^1A_1$)	(43)	c-$C_5H_5^+$ ($^1A_1$) + CH_4 → c-C_5H_6 + CH_3^+	47.65	264.0	
	(44)	c-$C_5H_5^+$ ($^1A_1$) + :CH_2 ($^3B_1$) → c-C_5H_4 ($^3B_1$) + CH_3^+	29.10	263.9	
		Average = $(1/N)\Sigma(\Delta H^o_{f,298})_i$ with $N = 2$		264.0	
c-$C_5H_5^+$ (D_{5h}, $^3A_1'$)	(45)	c-$C_5H_5^+$ ($^3A_1'$) → c-C_5H_4 ($^3B_1$)+ H^+	230.71	260.1	260.9[a]
	(46)	c-$C_5H_5^+$ ($^3A_1'$) + CH_3^- → c-C_5H_4 ($^3B_1$) + CH_4	−185.72	259.8	251.5[b]
		Average = $(1/N)\Sigma(\Delta H^o_{f,298})_i$ with $N = 2$		260.0	
c-$C_5H_5^-$ (D_{5h}, $^1A_1'$)	(47)	c-$C_5H_5^-$ + H^+ → c-C_5H_6	−352.20	18.6	
	(48)	c-$C_5H_5^-$ → c-$C_5H_5^{\bullet}$ + e^-	44.91	18.6	19.0 ± 2.0[c]
	(49)	c-$C_5H_5^-$ + CH_4 → c-C_5H_6 + CH_3^-	64.23	18.8	19.5 ± 2.4[d]
	(50)	c-$C_5H_5^-$ + $CH_3^{\bullet}$ → c-C_5H_6 + $CH_2^{\bullet-}$	56.43	19.1	
		Average = $(1/N)\Sigma(\Delta H^o_{f,298})_i$ with $N = 4$		18.8	
c-$C_5H_6^{\bullet+}$ (C_{2v}, $^2A_2$)	(51)	c-$C_5H_6^{\bullet+}$ + e^- → c-C_5H_6	−199.90	232.0	
	(52)	c-$C_5H_6^{\bullet+}$ + :CH_2($^1A_1$) → c-$C_5H_5^{\bullet}$ + CH_3^+	−7.91	230.4	
	(53)	c-$C_5H_6^{\bullet+}$ → c-$C_5H_5^{\bullet}$ + H^+	197.20	232.0	
		Average = $(1/N\Sigma(\Delta H^o_{f,298})_i$ with $N = 3$		231.5	
c-$C_5H_6^{\bullet-}$ (C_s, $^2A'$)	(54)	c-$C_5H_6^{\bullet-}$ → c-C_5H_6 + e^-	−25.98	58.1	
	(55)	c-$C_5H_6^{\bullet-}$ → c-$C_5H_4^{\bullet-}$ + H_2	24.38	57.7	
	(56)	c-$C_5H_6^{\bullet-}$ + CH_3^+ → c-$C_5H_5^{\bullet}$ + CH_4	−271.38	55.2	
	(57)	c-$C_5H_6^{\bullet-}$ + :CH_2 ($^1A_1$) → c-$C_5H_5^{\bullet}$ + CH_3^-	−60.06	53.9	
		Average = $(1/N)\Sigma(\Delta H^o_{f,298})_i$ with $N = 4$		56.2	

[a]Taken from Ref. 7.
[b]From Ref. 33.
[c]From Ref. 27.
[d]From Ref. 30.

($^3B_1$), c-$C_5H_5^{\bullet}$ and c-C_5H_6 (see Table 3). The calculated values of c-$C_5H_5^{\bullet}$ and c-C_5H_6 are in good agreement with the available experimental data from Refs 23–34. The discrepancies are 1–2 kcal mol^{-1} and the largest one is about 2 kcal mol^{-1} for the *EA*(c-$C_5H_5^{\bullet}$) value. The values obtained for *IP*, *EA* and *PA* are, respectively, 204.4, 42.5 and 230.7 kcal mol^{-1} for c-C_5H_4 ($^3B_1$), 197.7, 44.9 and 197.2 kcal mol^{-1} for c-$C_5H_5^{\bullet}$ and 199.9, 26.0 and 195.2 kcal mol^{-1} for c-C_5H_6 with a possible error of ±2 kcal mol^{-1}.

Next we calculated heats of formation for charged species of c-C_5H_4, c-$C_5H_5^{\bullet}$ and c-C_5H_6 (see Table 4). The heats of formation of c-$C_5H_4^{\bullet+}$, c-$C_5H_5^+$ ($^1A_1$), c-$C_5H_5^+$ ($^3A_1'$), c-$C_5H_5^-$, c-$C_5H_6^{\bullet+}$ and c-$C_5H_6^{\bullet-}$ were computed using three, two, two, four, three and four different working reactions, respectively. The values obtained are internally consistent. Our best estimates taken as the average are 329.9, 264.0, 260.0, 18.8, 231.5 and 56.2 kcal mol^{-1} for c-$C_5H_4^{\bullet+}$, c-$C_5H_5^+$ ($^1A_1'$), c-$C_5H_5^+$ ($^3A_1'$), c-$C_5H_5^-$, c-$C_5H_6^{\bullet+}$ and c-$C_5H_6^{\bullet-}$, respectively. The $\Delta H^o_{f,298}$(c-$C_5H_5^-$) value of 18.8 kcal mol^{-1} is in excellent agreement with available experimental data.

Table 5. Calculated C*—H bond dissociation energies (in kcal mol^{-1}) for c-$C_5H_5^{\bullet}$, c-$C_5H_5^+$,c-$C_5H_5^-$, c-C_5H_6, c-$C_5H_6^{\bullet+}$ and c-$C_5H_6^{\bullet-}$

Reaction No.	Reaction	Enthalpy of reaction	Reference
(58)	c-$C_5H_5^{\bullet}$ → c-C_5H_4 ($^3B_1$) + $H^{\bullet}$	112.3	
(59)	c-$C_5H_5^+$ ($^1A_1$) → c-$C_5H_4^{\bullet+}$ + $H^{\bullet}$	118.9	
(60)	c-$C_5H_5^+$ ($^3A_1'$) → c-$C_5H_4^{\bullet+}$ + $H^{\bullet}$	121.4	
(61)	c-$C_5H_5^-$ → c-$C_5H_4^{\bullet-}$ + $H^{\bullet}$	114.6	
(62)	c-C_5H_6 → c-$C_5H_5^{\bullet}$ + $H^{\bullet}$	83.5	83.6[a], 82.56[b]
(63)	c-$C_5H_6^{\bullet+}$ → c-$C_5H_5^+$ ($^1A_1$) + $H^{\bullet}$	81.3	
(64)	c-$C_5H_6^{\bullet+}$ → c-$C_5H_5^+$ ($^3A_1'$) + $H^{\bullet}$	78.8	
(65)	c-$C_5H_6^{\bullet-}$ → c-$C_5H_5^-$ + $H^{\bullet}$	12.6	

[a]Taken from Ref. 36.
[b]From Ref. 6f.

The difference between the calculated and experimental results is <1 kcal mol^{-1}, which lies in the error range of the experimental value, ± 2 kcal mol^{-1}. The $\Delta H^{o}_{f,298}$ (c-$C_5H_5^+$, D_{5h}, $^3A_1'$) value of 260.0 kcal mol^{-1} is in good agreement with that recently reported by Glukhovtsev *et al.*,[7] 260.7 kcal mol^{-1}, but it is about 8.5 kcal mol^{-1} higher than in experiment. As suggested by Glukhovtsev *et al.*,[7] this experimental estimate needs to be re-examined. It is worth mentioning that the symmetry of c-$C_5H_6^{\bullet -}$ is C_s in the ground electronic state. The C_{2v} structure of c-$C_5H_6^{\bullet -}$ is a transition state, which has one imaginary frequency both at the B3LYP/6–311G(d,p) and MP2/6–311G(d,p) levels of theory. The vibrational mode with imaginary frequency in the transition state is the rotation of CH_2 out of the molecular plane. Hence the C_{2v} geometry corresponds to a transition state between two degenerate C_s isomers. However, the energy of the C_{2v} structure is $\approx$0.5 kcal mol^{-1} lower than that of the C_s geometry at the CCSD(T)/6–311G(d,p), MP2/6–311+G (3df,2p) and G2M(RCC,MP2) levels, respectively, mainly owing to the thermal correction. This leads to the suggestion that the geometry of c-$C_5H_6^{\bullet -}$ is effectively C_{2v} symmetric.

In order to evaluate the strengths of C*—H bonds and to study the effect of the number of π-electrons on stabilization of the C*—H bonds (see Fig. 1), the C*—H dissociation energies for c-$C_5H_5^{\bullet}$, c-$C_5H_5^+$ ($^1A_1$), c-$C_5H_5^+$ ($^3A_1'$), c-$C_5H_5^-$, c-C_5H_6, c-$C_5H_6^{\bullet +}$, c-$C_5H_6^{\bullet -}$ were computed (see Table 5). The values obtained were 112.3, 118.9, 121.4, 114.6, 83.5, 81.3, 78.8 and 12.6 kcal mol^{-1}, respectively. The C*—H bond dissociation energy in c-C_5H_6 is 83.5 kcal mol^{-1}, which is in good agreement with the previously calculated[6f] and experimental[36] values. All values for the neutral and charged c-$C_5H_5^{\bullet}$ species vary in the range of $\approx$9 kcal mol^{-1} and those for neutral and charged c-C_5H_6 vary in the range of $\approx$4 kcal mol^{-1}, except for c-$C_5H_6^{\bullet}$. These results show that the change in the number of π-electrons in the ring by ± 1 has a moderate effect on the strength of the C*—H bond, unless aromatic stabilization occurs after breaking the C*—H bond. This is the case for the C*—H bond in c-$C_5H_6^{\bullet -}$, which is found to be very weak. The result can be attributed to the strong aromatic stabilization[37] of c-$C_5H_5^-$(D_{5h},$^1A_1'$), which has six π-electrons, as compared with c-$C_5H_6^{\bullet -}$, which has five π-electrons. In other cases, after H-splitting the number of π-electrons either does not change [c-$C_5H_5^-$ (6π) $\rightarrow$ c-$C_5H_4^{\bullet -}$ (6π); c- $C_5H_5^{\bullet}$ (5π) $\rightarrow$ c-C_5H_4, $^3B_1$ (5π); c-$C_5H_5^+$ (4π) $\rightarrow$ c-$C_5H_4^{\bullet +}$ (4π)] or the change does not lead to a large aromatic stabilization [c-C_5H_6 (4π) $\rightarrow$ c-$C_5H_5^{\bullet}$ (5π) and c-$C_5H_6^{\bullet +}$ (3π) $\rightarrow$ c-$C_5H_5^+$ (4π)].

Finally, it was also of interest to compare the singlet–triplet separation gap of cyclopentadienylidene with that of methylene (:CH_2). The values obtained were 6.1 and 3.7 kcal mol^{-1} for :CH_2 and c-C_5H_4 at the G2M(RCC,MP2) level, respectively. The former, 6.1 kcal mol^{-1} is about 3 kcal mol^{-1} lower than that in experiment, 9.0 kcal mol^{-1}.[17] However, if the 'higher level correction' is not included in the G2M(RCC,MP2) method, the computed values will be 9.3 and 6.8 kcal mol^{-1} for :CH_2 and c-C_5H_4, respectively. The value for :CH_2 is in good agreement with that in the experiment[17] and the theoretical value derived by Nguyen *et al.*[15] at the CCSD(T)/6–311++G(3df,2p) level, 9.6 kcal mol^{-1}. Since the singlet–triplet splitting is sensitive to the theoretical method, we recalculated this value for c-C_5H_4 at the CCSD(T)/6–311+G(3df,2p) level and obtained 7.7 kcal mol^{-1}, fairly close to the G2M(RCC,MP2) result without HLC. The singlet–triplet splitting of c-C_5H_4 can be also derived using the following isodesmic reaction:

$$\text{c-}C_5H_4(^3B_1) + CH_2(^1A_1) \rightarrow \text{c-}C_5H_4(^1A) + CH_2(^3B_1) \quad (6)$$

On the basis of heat of this reaction and the experimental singlet–triplet splitting of 9.0 kcal mol^{-1} for CH_2, the singlet–triplet separation energies of 6.6 and 7.0 kcal mol^{-1} for c-C_5H_4 are obtained at the G2M and CCSD(T)/6–311+G(3df,2p) levels, respectively. We can conclude that the singlet–triplet splitting in c-C_5H_4 is expected to be 7.0 ± 1.0 kcal mol^{-1}. Thus, the singlet–triplet separation gap of c-C_5H_4 is about 2.0 kcal mol^{-1} lower than that of :CH_2 and four π-electrons in the ring have a small effect on the singlet–triplet splitting.

CONCLUSIONS

The thermochemical parameters of c-C_5H_4 ($^3B_1$), c-$C_5H_5^{\bullet}$ and c-C_5H_6 were investigated at the G2M(RCC,MP2) level. The values obtained for the last two molecules are in excellent agreement with the available experimental data, with errors of ± 1 and ± 2 kcal mol^{-1} for the heat of formation and the other parameters, respectively. The present theoretical study suggests a heat of formation, ionization potential, electron affinity and proton affinity of 125.1, 204.4, 42.5 and 230.7 kcal mol^{-1}, respectively, for c-C_5H_4 ($^3B_1$), with the same possible errors as those for c-$C_5H_5^{\bullet}$ and c-C_5H_6. The heat of formation of c-$C_5H_4^{\bullet -}$ was evaluated as 82.0 kcal mol^{-1}, about 10 kcal mol^{-1} higher than in experiment. This leads to the suggestion that the experimental $\Delta H^{o}_{f,298}$(c-$C_5H_4^{\bullet -}$) value needs to be re-examined.

Acknowledgements

This work was supported by Academia Sinica and in part by the National Science Council of ROC under Grant NSC 8902113-M-001-069. T.L.N. and T.N.L. are grateful to IAMS for visiting fellowship.

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