Computational Study on the Thermochemistry of Cyclopentadiene Derivatives and Kinetics of Cyclopentadienone Thermal Decomposition

Hai Wang*

Department of Mechanical Engineering, University of Delaware, Newark, Delaware 19716-3140

Kenneth Brezinsky

Department of Chemical Engineering, University of Illinois at Chicago, Chicago, Illinois 60607

Received: August 28, 1997; In Final Form: December 5, 1997

The enthalpies of formation were determined for 15 intermediate species of cyclopentadiene oxidation under combustion conditions by ab initio molecular orbital calculations at the G2(MP2,SVP) and G2(B3LYP/MP2,SVP) levels of theory and with the use of isodesmic reactions. The G2(B3LYP/MP2,SVP) method, a hybrid of G2(MP2,SVP) and the density-function-based G2(B3LYP/MP2), was devised in the present study. The devised method is less demanding computationally, but it provides atomization energies with accuracy comparable with G2(MP2) and G2(B3LYP/MP2). In addition, the pathways and reaction rate coefficients for the thermal decomposition of cyclopentadienone were studied with molecular orbital and RRKM calculations. The computational results show that at high temperatures the decomposition of cyclopentadienone leads primarily to cyclobutadiene. An analysis of the chemically activated reactions of the cyclopentadienyl radical suggests that cyclopentadienylidene may potentially be an important intermediate species of cyclopentadiene oxidation at high temperatures.

I. Introduction

It has been well-established that during the high-temperature oxidation of benzene and toluene one of the major intermediates is cyclopentadiene (C_5H_6).[1,2] The cyclopentadiene may then be oxidized to cyclopentadienone (C_5H_4O), which subsequently decomposes to noncyclic species, such as acetylene, diacetylene, and possibly vinylacetylene.

Detailed kinetic models assembled on the basis of the aforementioned reaction pathway have been tested against available experimental data, including the species profiles measured during benzene and toluene oxidation in a flow reactor over the temperature range 1000−1200 K,[2] the species profiles in the burner-stabilized low-pressure benzene flame[3−5] of Bittner and Howard,[6] and the laminar flame speeds of benzene−air and toluene−air mixtures.[7,8] It was shown that the models predicted reasonably well each individual set of the experimental data, but a comprehensive and physically justifiable model, which is capable of closely predicting *all* the available experimental data, is still lacking.

The inability of the detailed kinetic models to reconcile various literature data can be attributed at least partly to the uncertainties in the thermodynamic data. There are few experimental data available for the enthalpy of formation, $\Delta_f H_{298}°$, of the intermediate chemical species involved in the pathway of aromatics oxidation via cyclopentadiene. In particular, the uncertainty in the $\Delta_f H°_{298}$ of the cyclopentadienyl radical is as large as ±10 kcal/mol. Furthermore, measurements for the oxygenated species are not at all available. Karni et al.[9] performed ab initio molecular orbital (MO) calculations at the Hartree−Fock level of theory, employing the 3-21G and 6-31G(d) basis sets. With the use of isodesmic reactions, they estimated the thermochemical data of cyclopentadiene derivatives. These data are valuable in that they have been used as the basis for the subsequent development of detailed kinetic models of one-ring aromatics oxidation.

Because of the limited predictive accuracy of the Hartree−Fock method[10] and considering the recent developments of more predictive computational chemistry tools, the accuracy of the earlier thermochemistry estimates of ref 9 should be and can be improved. We note that the G2 method[11] and its variations[12−15] are capable of predicting the atomization energies with an average error of less than 2 kcal/mol. Because the prediction of atomization energy is a more stringent test than the prediction of enthalpy of formation with the use of isodesmic reactions, it is expected that the G2 methods can predict $\Delta_f H°_{298}$ to within ±2 kcal/mol accuracy. These methods have been used to predict $\Delta_f H°_{298}$ for strained ring compounds.[16−18]

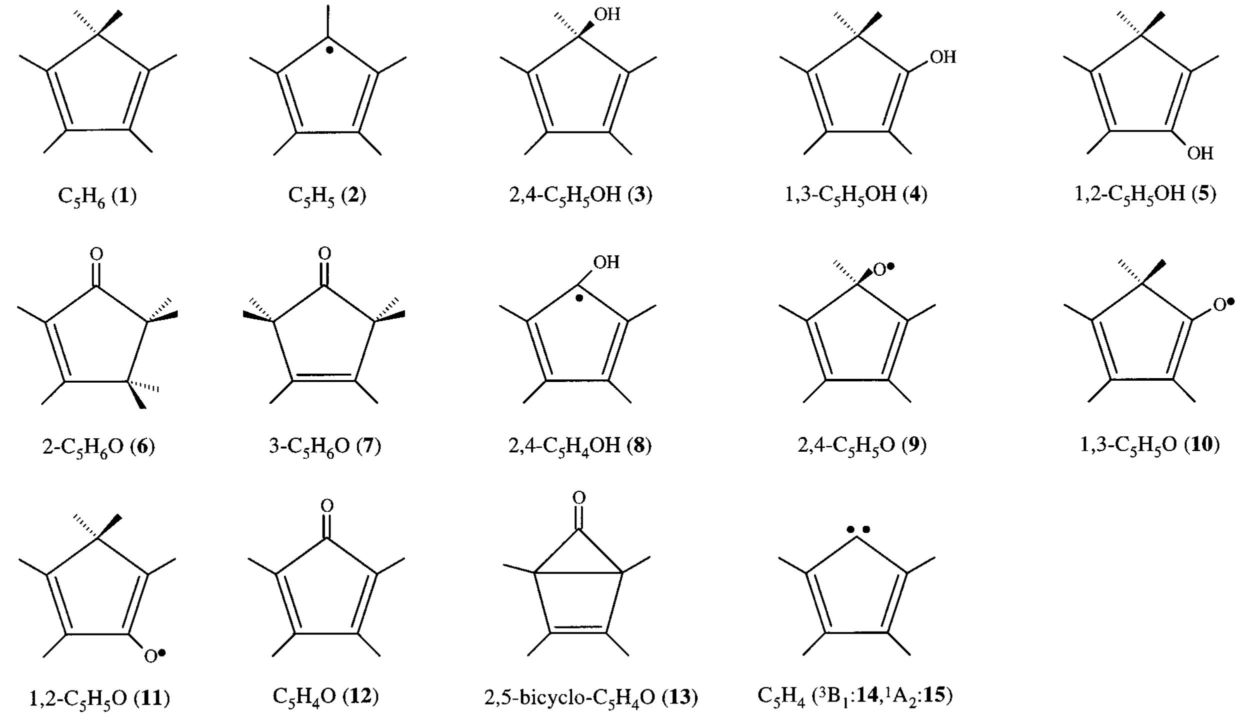
In this study, we used several simplified versions of G2 to determine the enthalpies of formation for the cyclopentadiene and cyclopentadiene derivatives. The target species are shown in Figure 1 and include cyclopentadiene (C_5H_6, **1**), cyclopentadienyl (C_5H_5, **2**), cyclopentadienol (C_5H_5OH, **3-5**), cyclopentenone (C_5H_6O, **6** and **7**), C_5H_5O radical species (**8**−**11**), cyclopentadienone (C_5H_4O, **12**), oxobicyclopentene (C_5H_4O, **13**), and the triplet and singlet cyclopentadienylidene (**13**, **14**) radicals.

In addition to the critical importance of accurate thermochemical data in kinetic model development, we note that there still exist uncertainties in the reaction pathways leading to ring breakage. In particular, it was proposed[2] that one of the major steps of ring breakdown is the thermal decomposition of **12**, $C_5H_4O \rightarrow CO + 2C_2H_2$. It was identified in modeling studies

---

* Corresponding author: Department of Mechanical Engineering, University of Delaware, 102C Spencer Laboratory, Newark, DE 19716-3140. E-mail: hwang@me.udel.edu. FAX: (302) 831-3619.

S1089-5639(97)02826-0 CCC: $15.00



C_5H_6 (**1**) C_5H_5 (**2**) 2,4-C_5H_5OH (**3**) 1,3-C_5H_5OH (**4**) 1,2-C_5H_5OH (**5**)

2-C_5H_6O (**6**) 3-C_5H_6O (**7**) 2,4-C_5H_4OH (**8**) 2,4-C_5H_5O (**9**) 1,3-C_5H_5O (**10**)

1,2-C_5H_5O (**11**) C_5H_4O (**12**) 2,5-bicyclo-C_5H_4O (**13**) C_5H_4 ($^3B_1$:**14**,$^1A_2$:**15**)

Figure 1. Structures of the target species.

of benzene and toluene oxidation in a flow reactor[2] and in laminar flames burning benzene− and toluene−air mixtures[7] that the above reaction was one of the dominant ring breakdown processes. Because the proposed reaction requires breaking three chemical bonds, it must involve one or more thermally activated isomers before it can form the final products. A detailed knowledge of the minimum-energy paths is therefore extremely valuable. Hence, we performed molecular orbital calculations to determine the energy barriers along several possible paths. On the basis of the computed energy barriers and vibrational frequencies, we calculated the pressure-dependent rate coefficients using the Rice−Ramsperger−Kassel−Marcus (RRKM) theory.[19] In addition, the reaction pathways of several chemically activated reactions of the cyclopentadienyl radical are discussed. The emphasis was placed on the cyclopentadienylidene radical as a potential intermediate of aromatics oxidation.

II. Computational Methodology

The ab initio MO calculations were carried out using the Gaussian 94 program.[20] We adopted the G2[11] and G2(MP2)[12] methods for cyclopentadiene (**1**) and cyclopentadienone (**12**), G2(MP2) for 2,4-cyclopentadien-1-ol (**3**), and G2(MP2,SVP) for all target species. The last method presents significant saving in computational resources without significant sacrifice in accuracy, as will be demonstrated by comparing the obtained results with the more expansive G2 and G2(MP2).

To further explore savings in computational resources, we propose to combine the reduced basis-set approach of ref 13, e.g., G2(MP2,SVP), and the density-function-based geometry and frequencies of Bauschlisher and Partridge,[15] i.e., G2(B3LYP/MP2). A hybrid of the two approaches is denoted as G2-(B3LYP/MP2,SVP). Specifically, we optimize the geometry and compute the vibrational frequencies using the B3LYP method[21] with the split-valence plus polarization 6-31G(d) basis set. We then performed the QCISD(T) calculation with the 6-31G(d) basis and the MP2 calculation with the 6-311+G(3df,2p) basis set. The resulting G2(B3LYP/MP2,SVP) energy is given by

$$E_0 = E[\mathrm{QCISD(T)/6\text{-}31G(d)}] + \Delta_{\mathrm{B3LYP/MP2,SVP}} + \mathrm{HLC} + E(\mathrm{ZPE})$$

where $\Delta_{\mathrm{B3LYP/MP2,SVP}} = E[\mathrm{MP2/6\text{-}311{+}G(3df,2p)}] - E[\mathrm{MP2/6\text{-}31G(d)}]$, and E(ZPE) is the zero-point energy determined from the B3LYP/6-31G(d) frequencies multiplied by a scaling factor of 0.98.[15] Such an approach is similar to G2(MP2,SVP), but the MP2 geometries and vibrational frequencies are replaced by those of B3LYP calculations.

For the higher level correction,

$$\mathrm{HLC} = -An_\beta - Bn_\alpha$$

where n_α and n_β are respectively the number of α and β valence electrons, we assigned $B = 0.0019$ au, which is the same as that of G2[11] and G2(MP2)[12] because it is based on the H atom. To obtain the A value, we performed calculations and minimized the average deviation between the computed and experimental dissociation energies for the 55 species originally used in the G2 study. The value of A determined in this manner is 0.005 19 au.

To estimate the enthalpies of formation, each target species was assigned with one or more isodesmic reactions.[22] The reaction enthalpies were computed from the energy difference between the products and reactants. The enthalpies of formation of the reference species in an isodesmic reaction were obtained through a review of literature data.

The transition-state structures of cyclopentadienone thermal decomposition were initially optimized with the spin-unrestricted Hartree−Fock (UHF) method, employing the split-valence 3-21G basis set. The structures were further optimized at the HF/6-31G(d) level and refined at the UMP2(full)/6-31G(d) level. In all calculations, we employed the analytical gradient procedure and the combined synchronous transit and quasi-Newton (STQN) method.[23] The vibrational frequencies were obtained

TABLE 1: Summary of the G2(B3LYP/MP2,SVP) Energies (*E*, Hartrees)

molecule	*E*	molecule	*E*	molecule	*E*
Be	−14.625 413	CO_2	−188.358 996	NH_3	−56.456 075
C	−37.782 390	CS	−435.706 871	NO	−129.736 637
Cl	−459.667 800	C_2H_2	−77.184 968	N_2	−109.393 237
F	−99.630 172	C_2H_4	−78.412 466	N_2H_4	−111.676 867
H	−0.500 000	C_2H_6	−79.624 002	NaCl	−621.672 526
Li	−7.432 217	ClF	−559.396 102	Na_2	−323.723 592
N	−54.517 119	ClO	−534.745 718	OH	−75.641 695
Na	−161.846 168	Cl_2	−919.428 002	O_2	−150.145 117
O	−74.980 218	F_2	−199.318 601	PH_2	−342.043 926
P	−340.814 151	HCN	−93.284 061	PH_3	−342.673 612
Si	−288.930 385	HCO	−113.696 041	P_2	−681.813 592
S	−397.647 653	HCl	−460.332 869	SO	−472.820 514
BeH	−15.193 265	HF	−100.348 066	SO_2	−548.011 396
CH	−38.410 467	HOCl	−535.398 936	S_2	−795.453 632
$CH_2(^1A_1)$	−39.056 247	CH_2O	−114.335 692	$SiH_2(^1A_1)$	−290.163 340
$CH_2(^3B_1)$	−39.065 791	H_2O	−76.329 947	$SiH_2(^3B_1)$	−290.126 096
CH_3	−39.740 765	H_2O_2	−151.362 068	SiH_3	−290.767 891
CH_3Cl	−499.543 302	H_2S	−398.924 832	SiH_4	−291.411 917
CH_4	−40.406 254	LiF	−107.281 589	SiO	−364.215 087
CH_3OH	−115.529 605	LiH	−8.021 004	Si_2	−577.977 725
CH_3SH	−438.139 766	Li_2	−14.906 856	Si_2H_6	−581.656 192
CN	−92.583 933	NH	−55.140 325		
CO	−113.176 597	NH_2	−55.786 818		

TABLE 2: Summary of the Computed G2(B3LYP/MP2,SVP) D_0 Values (kcal/mol). Δ Is the Experimental Results Minus the Theoretical Results

molecule	D_0	Δ[a]	molecule	D_0	Δ[a]
BeH	42.6	4.3	H_2S	173.8	−0.6
CH	80.3	−0.4	LiF	137.5	0.1
$CH_2(^1A_1)$	171.7	−1.1	LiH	55.7	0.3
$CH_2(^3B_1)$	177.7	1.9	Li_2	26.6	−2.6
CH_3	287.5	1.7	NH	77.3	1.7
CH_3Cl	372.0	−1.0	NH_2	169.1	0.9
CH_4	391.3	1.2	NH_3	275.3	1.4
CH_3OH	481.0	−0.2	NO	150.1	0.0
CH_3SH	445.1	0.0	N_2	225.1	0.0
CN	178.4	−1.8	N_2H_4	403.0	2.4
CO	259.6	−3.4	NaCl	99.4	−1.9
CO_2	386.4	−4.5	Na_2	19.6	−3.0
CS	173.6	−4.1	OH	101.3	0.0
C_2H_2	389.0	−0.1	O_2	115.8	2.2
C_2H_4	531.6	0.3	PH_2	144.1	0.6
C_2H_6	664.3	2.0	PH_3	225.4	2.0
ClF	61.5	−1.2	P_2	116.2	−0.1
ClO	61.3	2.0	SO	120.8	2.7
Cl_2	57.9	−0.7	SO_2	252.9	1.1
F_2	36.5	0.4	S_2	99.3	1.4
HCN	303.9	−2.1	$SiH_2(^1A_1)$	146.1	−1.7
HCO	271.8	−1.5	$SiH_2(^3B_1)$	122.7	0.7
HCl	103.5	−1.3	SiH_3	211.7	2.3
HF	136.7	−1.5	SiH_4	302.0	0.8
HOCl	157.4	−1.1	SiO	191.0	−0.5
CH_2O	359.4	−2.1	Si_2	73.3	0.7
H_2O	219.3	0.0	Si_2H_6	498.8	1.3
H_2O_2	251.9	0.4			

[a] Average error = 1.37 kcal/mol.

from the geometries optimized at the UMP2(full)/6-31G(d) level of theory. These frequencies are multiplied by an appropriate scaling factor of 0.9646.[24] The energy barriers were determined by the G2(MP2,SVP) energies. For comparison, G2(B3LYP/MP2,SVP) was also employed for selected transition-state calculations.

III. Results and Discussion

The G2(B3LYP/MP2,SVP) Method. Table 1 presents the total energies computed with G2(B3LYP/MP2,SVP). The resulting dissociation energies and the differences between the experimental and theoretical dissociation energies are shown in Table 2. The G2(B3LYP/MP2,SVP) method yields an average error of 1.37 kcal/mol and a maximum error of 4.5 kcal/mol for dissociation energy. These results are nearly identical with the respective average and maximum deviations of G2-(MP2) at 1.31 and 4.2 kcal/mol,[12] G2(MP2,SVP) at 1.34 and 4.2 kcal/mol,[13] and G2(B3LYP/MP2) at 1.32 and 3.7 kcal/mol.[15] At the same time, we note that G2(B3LYP/MP2,SVP) presents significant savings in both CPU time and disk storage requirements, because the QCISD(T)/6-311G(d,p) calculation in G2-(MP2) and G2(B3LYP/MP2) was replaced with the significantly less demanding QCISD(T)/6-31G(d) calculation. The computational time required for G2(B3LYP/MP2,SVP) is roughly a factor of 10 less than G2, one-fifth comparing to G2(MP2), and one-half of that of G2(MP2,SVP).

Enthalpies of Formation. Table 3 presents the G2 energies of the target and reference species and the literature enthalpy values of the reference species used for determination of the $\Delta_f H°_{298}$ of the target species. When available, the uncertainties in the reference $\Delta_f H°_{298}$ are also provided.

Table 4 presents the isodesmic reactions assigned and the enthalpies of formation obtained for the target species. It is seen that for C_5H_6 (**1**), 2,4-C_5H_5OH (**3**), and 2,5-C_5H_4O (**12**) the $\Delta_f H°_0$ values predicted with the employed methods are within 1 kcal/mol of each other, including G2 for **1** and **12**. The remarkable agreement suggests that calculations performed at the G2(MP2,SVP) and G2(B3LYP/MP2,SVP) levels of theory are as accurate as the full G2 method. Hence, other target species were studied only with the latter two methods, which provide nearly identical enthalpy of formation for almost every species studied. The agreement in the results obtained with G2-(MP2,SVP) and G2(B3LYP/MP2,SVP) provides additional confidence that the estimated enthalpies of formation are accurate. The only exception is that of **9**, in that we were not able to obtain meaningful QCISD(T)/6-31G(d) and MP2/6-311+G(3df,2p) energies when the optimized B3LYP/6-31G-(d) geometry was used to compute the G2(B3LYP/MP2,SVP) energy.

Averaging the $\Delta_f H°_0$ results shown in columns 3−6 of Table 4 and correcting them to 298 K by sensible enthalpies, we obtained $\Delta_f H°_{298}$ of the target species, as presented in Table 4. These $\Delta_f H°_{298}$ values are recommended for future uses. For

TABLE 3: Calculated G2, G2(MP2), G2(MP2,SVP), and G2(B3LYP/MP2,SVP) Total Energies (Hartrees) and Enthalpies of Formation of Reference Species (kcal/mol)

	G2	G2(MP2)	G2(MP2,SVP)	G2(B3LYP/MP2,SVP)	$\Delta_f H°_{298}$	$\Delta_f H°_0$
reference species						
CH_4	−40.410 89	−40.409 66	−40.407 68	−40.4062 5[a]	−17.9 ± 0.1[b]	−15.9[b]
C_2H_4	−78.415 93	−78.414 30	−78.413 44	−78.4124 7[a]	12.5 ± 0.1[b]	14.6[b]
C_2H_6	−79.630 86	−79.628 91	−79.626 06	−79.6240 0[a]	−20.0 ± 0.1[c]	−16.3[d]
C_2H_5			−78.965 60	−78.964 10	28.4 ± 0.2[e]	30.5[d]
C_2H_5OH		−154.760 50	−154.758 19	−154.756 90	−56.2 ± 0.1[c]	−52.0[f]
CH_3CHOH			−154.107 22	−154.106 34	−14.5[g]	−11.3[d]
CH_3CH_2O			−154.089 75	−154.088 34	−3.7 ± 0.8[h]	−0.4 ± 0.9[h]
CH_2CHOH			−153.553 63	−153.553 08	−29.8[i]	−27.3[d]
CH_2CHO			−152.919 07	−152.919 02	6.1[j]	7.8[d]
CH_3CHO	−153.576 84	−153.572 97	−153.571 48	−153.571 01	−39.7 ± 0.1[c]	−37.2[d]
CH_2 ($^3B_1$)			−39.066 23	−39.0657 9[a]	93.8[j]	93.7[d]
CH_2 ($^1A_1$)			−39.056 34	−39.0562 5[a]	102.7[j]	102.6[d]
i-C_4H_{10}			−158.076 63		−32.1 ± 0.2[b]	−25.2[d]
target species						
C_5H_6 (**1**)	−193.707 33	−193.703 69	−193.704 25	−193.703 08	32.1 ± 0.4[c]	36.2[d]
C_5H_5 ($^2B_1$) (**2**)			see text	−193.072 07		
C_5H_5 ($^2A_2$) (**2**)			see text	−193.071 04		
2,4-cyclo-C_5H_5OH (**3**)		−268.830 40	−268.831 21	−268.830 80		
1,3-cyclo-C_5H_5OH (**4**)			−268.843 27	−268.842 42		
1,2-cyclo-C_5H_5OH (**5**)			−268.844 55	−268.843 77		
2-cyclo-C_5H_6O (**6**)			−268.865 95	−268.865 02		
3-cyclo-C_5H_6O (**7**)			−268.860 10	−268.859 42		
2,4-cyclo-1-C_5H_4OH (**8**)			−268.219 85	−268.221 09		
2,4-cyclo-1-C_5H_5O (**9**)			−268.160 75	k		
1,3-cyclo-1-C_5H_5O (**10**)			−268.232 09	−268.231 26		
1,2-cyclo-1-C_5H_5O (**11**)			−268.216 30	−268.218 66		
2,4-cyclo-C_5H_4O (**12**)	−267.653 02	−267.647 27	−267.648 48	−267.648 55		
bicyclo-C_5H_4O (**13**)			−267.568 17	−267.568 49		
c-C_5H_4 (**14**) ($^3B_1$)			−192.391 81	−192.392 54		
c-C_5H_4 (**15**) ($^1A_2$)			−192.386 49	−192.387 21		

[a] From Table 2. [b] Reference 25. [c] Reference 26. [d] Corrected to 0 K with the sensible enthalpy ($H°_{298} - H_0°$). Hindered internal rotation is taken into consideration when necesssary. [e] Reference 27. [f] Corrected to 0 K with the sensible enthalpy ($H°_{298} - H_0°$) value of ref 28. [g] Reference 29. [h] Reference 30. [i] Reference 31. [j] Reference 32. [k] Unable to obtain meaningful MP2/6-311+G(3df,2p) and QCISD(T)/6-31G(d) energies.

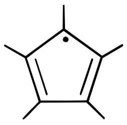
TABLE 4: Enthalpies of Formation of Target Species (kcal/mol)

		$\Delta_f H°_0$				average		literature
species	isodesmic reaction	G2	G2(MP2)	G2(MP2, SVP)	G2(B3LYP/ MP2,SVP)	$\Delta_f H°_0$[a]	$\Delta_f H°_{298}$[b]	$\Delta_f H°_{298}$
C_5H_6 (**1**)	$+ 5CH_4 = 3C_2H_6 + 2C_2H_4$	36.4	36.8	36.2	36.3	36.4	32.3	32.1 ± 0.4[d], 33.3[e]
C_5H_5 ($^2B_1$) (**2**)	$+ 5CH_4 = C_2H_5 + 2C_2H_6 + 2C_2H_4$			see text	65.0	65.0[c]	62.0	63 ± 2,[f] 61 ± 2,[g] 50,[h] 58 ± 2,[i] 63.2[e]
C_5H_5 ($^2A_2$) (**2**)				see text	65.6	65.6[c]	62.6	
2,4-C_5H_5OH (**3**)	$+ 5CH_4 = 2C_2H_6 + C_2H_5OH + 2C_2H_4$		4.2	3.8	3.9	3.8	−0.6	1.9[e]
	$+ C_2H_6 = C_5H_6$(**1**) $+ C_2H_5OH$		3.6	3.7	3.8			
1,3-C_5H_5OH (**4**)	$+ 5CH_4 = 3C_2H_6 + CH_2CHOH + C_2H_4$			−4.9	−4.8	−4.9	−9.2	−5.8[e]
	$+ C_2H_4 = C_5H_6$(**1**) $+ CH_2CHOH$			−5.0	−4.9			
1,2-C_5H_5OH (**5**)	$+ 5CH_4 = 3C_2H_6 + CH_2CHOH + C_2H_4$			−5.7	−5.6	−5.8	−10.0	−6.5[e]
	$+ C_2H_4 = C_5H_6$(**1**) $+ CH_2CHOH$			−5.9	−5.8			
2-C_5H_6O (**6**)	$+ 5CH_4 = 3C_2H_6 + CH_3CHO + C_2H_4$			−17.9	−17.6	−17.8	−22.2	
3-C_5H_6O (**7**)	$+ 5CH_4 = 3C_2H_6 + CH_3CHO + C_2H_4$			−14.2	−14.1	−14.2	−18.7	
2,4-C_5H_4OH (**8**)	$+ 5CH_4 = 2C_2H_6 + CH_3CHOH + 2C_2H_4$			19.6	19.0	19.3	15.9	20.9[e]
	$+ C_2H_6 = C_5H_6$(**1**) $+ CH_3CHOH$			19.6	18.8			
2,4-C_5H_5O (**9**)	$+ 5CH_4 = 2C_2H_6 + CH_3CH_2O + 2C_2H_4$			56.6		56.6	52.8	54.1[e]
	$+ C_2H_6 = C_5H_6$(**1**) $+ CH_3CH_2O$			56.6				
1,3-C_5H_5O (**10**)	$+ 5CH_4 = 3C_2H_6 + CH_2CHO + C_2H_4$			15.5	16.0	15.7	12.2	14.3[e]
	$+ C_2H_4 = C_5H_6$(**1**) $+ CH_2CHO$			15.5	15.8			
1,2-C_5H_5O (**11**)	$+ 5CH_4 = 3C_2H_6 + CH_2CHO + C_2H_4$			25.4	23.9	24.6	21.1	24.7[e]
	$+ C_2H_4 = C_5H_6$(**1**) $+ CH_2CHO$			25.4	23.7			
C_5H_4O (**12**)	$+ 5CH_4 = 2C_2H_6 + CH_3CHO + 2C_2H_4$	15.6	16.2	16.1	16.4	16.0	13.2	
	$+ C_2H_6 = C_5H_6$(**1**) $+ CH_3CHO$	15.5	15.6	16.0	16.3			
bicyclo-C_5H_4O (**13**)	$+ 2C_2H_6 = 2i\text{-}C_4H_{10} + CH_3CHO + C_2H_4$		66.8		66.8	64.1		
C_5H_4 ($^3B_1$) (**14**)	$+ 6CH_4 = CH_2(^3B_1) + 3C_2H_6 + 2C_2H_4$			127.6	127.2	127.4	125.2	112.3 ± 4.7[j]
C_5H_4 ($^1A_2$) (**15**)	$+ 6CH_4 = CH_2(^1A_1) + 3C_2H_6 + 2C_2H_4$			133.7	133.4	133.6	131.6	118.1 ± 4.7[j]

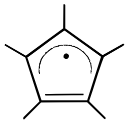
[a] Average over calculated $\Delta_f H°_0$ values. [b] Corrected from 0 K. [c] $\Delta_f H°_0$ from G2(B3LYP/MP2,SVP) calculations only. [d] Reference 26. [e] Computed, ref 9. [f] Reference 33. [g] From measurements of cyclopentadiene acidity[34] and electron affinity.[35] [h] Reference 36. [i] Reference 37. [j] Reference 38, based on the sum of $\Delta_f H°_{298}$ of c-$C_5H_4^-$ = 71.9 kcal/mol[38,39] and the electron photodetachment (EPD) thresholds of c-$C_5H_4^-$.[38] See text for further discussion.

comparison, available literature data are also shown in Table 4. It is seen that the computed $\Delta_f H°_{298}$ of C_5H_6 (**1**) is 32.3 kcal/mol, which is in close agreement with that recommended by Pedley et al.,[26] i.e., 32.1 ± 0.4 kcal/mol. This is the only reliable data available among the target species. A comparison between the results of ref 9 and the present study shows that the $\Delta_f H^\circ_{298}$ of ref 9 are consistently larger, with the largest and average differences equal to 5 and 2.5 kcal/mol, respectively.

The Cyclopentadienyl Radical. The cyclopentadienyl radical is a Jahn−Teller species. The ground-state C_5H_5 does not assume D_{5h} symmetry and resorts to C_{2v} symmetry.[40,41] Two initial guesses were generated for geometry optimization, including



$^2B_1$



$^2A_2$

The optimization results are seen to be inconsistent when different levels of theory were employed. Specifically, the UHF/6-31G(d) calculation yielded a local minimum corresponding to the $^2B_1$ wave function, but it considers the wave function $^2A_2$ to be unstable. Both UMP2(full)/6-31G(d) and CISD/6-31G(d) levels of theory yield a saddle point for the $^2B_1$ wave function (exactly one imaginary frequency) and again consider the $^2A_2$ wave function to be unstable. We note that the discrepancy between UMP2 and HF results for the $^2B_1$ wave function renders its G2(MP2,SVP) energy meaningless. As such, the result is omitted from Tables 3 and 4.

The density functional theory at the B3LYP level considers both wave functions to be stable. Such a result was found to be independent of the basis set employed, from the modest 6-31G(d) to the expansive 6-311++G(3df,2p). The optimized geometries are found to be the local minima of the potential energy surface (PES) of each wave function. The B3LYP energies of $^2B_1$ and $^2A_2$ are nearly equal. In addition, the G2-(B3LYP/MP2,SVP) energies are also nearly identical. Hence, despite the problems encountered in MP2 and CISD calculations, we used the G2(B3LYP/MP2,SVP) energies to compute the enthalpies of formation of C_5H_5. The resulting $\Delta_f H^\circ_{298}$ is 62.0 kcal/mol for the $^2B_1$ wave function and 62.6 kcal/mol for $^2A_2$. On the basis of these results, we recommend an enthalpy of formation of 62 kcal/mol for C_5H_5. This value is in close agreement with 63 ± 2 kcal/mol reported by Defrees et al.[33] and 61 ± 2 kcal/mol from the measurements of cyclopentadiene acidity[34] and electron affinity.[35] However, the recommended value is larger than $\Delta_f H^\circ_{298} = 58 \pm 2$ kcal/mol, evaluated from the kinetics of cyclopentadiene iodination.[37]

We note that the results presently obtained for C_5H_5 can do no more than confirm the earlier results of Borden and Davidson,[42] who performed π-space CI calculation using a basis set of STO-3G orbitals. In that study, Borden and Davidson demonstrated that $^2B_1$ and $^2A_2$ wave functions have almost exactly the same energy at their respective minimum energy geometries. Moreover, they suggested that the $^2B_1$ and $^2A_2$ wave functions can nearly freely isomerize without an appreciable energy barrier. If so, we would expect the existence of a small vibrational frequency for both wave functions. This is indeed the case, as the B3LYP calculations yielded a vibrational frequency (20−100 cm^{-1}) for both wave functions, irrespective of the basis function employed. Such a vibrational frequency was found to correspond to ring distortion. We note that the Hartree−Fock calculation for the $^2B_1$ wave function does not yield this small frequency.

In hope of obtaining the PES between the two wave functions, we performed extensive calculations using the internal reaction coordinate (IRC) method.[43] However, we were not able to obtain a complete PES, because the flatness of the potential energy surface prohibits gradient-based minimization techniques to reach a local minimum when the symmetry constraint was removed. Nonetheless, limited results obtained by us further suggest that the internal isomerization is extremely facile, in that a distortion from the C_{2v} symmetry does not lead to any appreciable rise in energy (<0.1 kcal/mol).

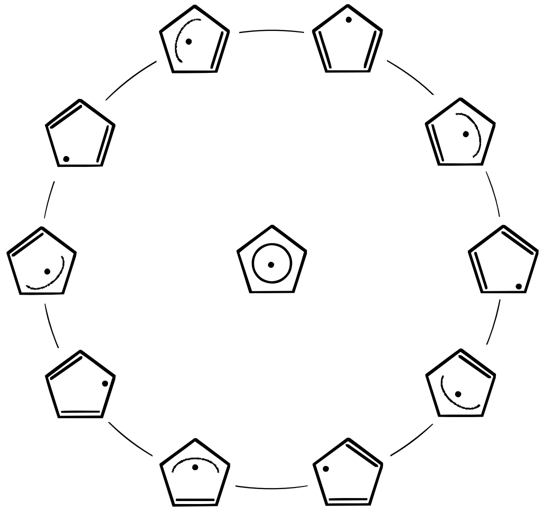


Figure 2. Pseudorotation in the cyclopentadienyl radical.[42]

Rotational Constants and Vibrational Frequencies. Table 5 presents the rotational constants and the vibrational frequencies computed at the B3LYP/6-31G(d) level of theory. We found that the frequencies from B3LYP/6-31G(d) calculations are very close to the MP2(full)/6-31G(d) results, as shown in Table 5 for C_5H_4O and bicyclo-C_5H_4O. The differences in the evaluated specific heats and entropies are negligibly small between the MP2 and B3LYP frequencies.

The facile internal isomerization of the $^2B_1$ and $^2A_2$ wave functions requires the entropy of C_5H_5 to be evaluated with additional care. Figure 2 shows how this internal isomerization might take place. It is seen that the isomerization can yield a pseudorotation within the C_5H_5 structure, which would proceed without an appreciable hindrance as suggested by Borden and Davidson.[42] Such a pseudorotation is supported by the experimental electron spin resonance (ESR) spectrum of the C_5H_5 radical down to 120 K,[44] which was found frozen out at 70 K on the ESR time scale. If one assumes that the latter temperature corresponds to the energy barrier of the internal pseudorotation, it would produce a negligible hindrance energy of 0.14 kcal/mol.

The previously discussed vibrational modes with ultralow wave numbers (at 26 and 57 cm^{-1} for the respective wave functions $^2B_1$ and $^2A_2$; see Table 5) mirror the pseudorotation mode, which are expected to be highly anharmonic. It is better to approximate such an internal degree of freedom by an internal rotor. Its moment of inertia can be approximated by considering that the pseudorotation resembles the external rotor with the rotational axis perpendicular to the C_5H_5 ring. Such a treatment would cause the entropy of C_5H_5 to increase by as much as 6−7 cal mol^{-1} s^{-1} from that previously found. For example, S°_{298} determined with the pseudorotor treatment is 73.5 cal mol^{-1} s^{-1}, compared to the compilation of Burcat et al.[32] at 66.8 cal mol^{-1} s^{-1}.

Potential Energy Surface of Cyclopentadienone Decomposition. It is fairly well agreed that one of the ring-breaking processes during benzene oxidation occurs with cyclopentadi-

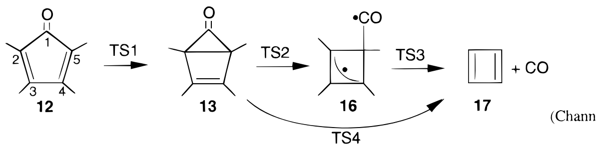
TABLE 5: Molecular Properties Computed at the B3LYP/6-31G(d) Level of Theory

species	rotational constants (cm^{-1})			vibrational frequencies[a] (cm^{-1})													
C_5H_6	0.282	0.274	0.142	343	511	675	697	797	797	912	913	931	937	959	1002	1102	1111
				1118	1258	1305	1391	1419	1544	1629	2965	2988	3144	3155	3173	3179	
C_5H_5 ($^2B_1$)	0.309	0.283	0.148	26	494	507	675	705	802	827	869	877	917	936	1048	1065	1130
				1205	1285	1381	1480	1527	3158	3163	3174	3190	3197				
C_5H_5 ($^2A_2$)	0.310	0.283	0.148	57	483	518	673	705	803	828	861	883	909	959	1026	1073	1130
				1203	1285	1390	1441	1563	3160	3161	3175	3190	3198				
2,5-C_5H_5OH	0.247	0.120	0.087	181	271	319	544	551	680	706	779	827	874	936	941	978	1014
				1066	1097	1141	1175	1275	1302	1369	1400	1568	1642	2864	3144	3157	3170
				3188	3663												
1,3-C_5H_5OH	0.274	0.114	0.082	225	252	385	409	501	618	664	793	825	883	908	938	948	1001
				1108	1123	1171	1221	1282	1331	1393	1433	1579	1674	2962	2991	3148	3181
				3186	3687												
1,2-C_5H_5OH	0.271	0.114	0.081	222	265	369	393	600	623	658	752	792	902	908	912	924	987
				1091	1108	1168	1237	1272	1312	1411	1429	1572	1686	2959	2979	3131	3175
				3193	3691												
2-C_5H_6O	0.247	0.119	0.083	106	290	452	534	617	745	760	811	823	907	975	993	1017	1098
				1146	1170	1220	1250	1314	1355	1452	1484	1632	1780	2982	3006	3018	3056
				3138	3179												
3-C_5H_6O	0.246	0.120	0.083	93	374	454	457	605	669	760	760	822	952	96	966	997	1115
				1121	1121	1175	1272	1283	1368	1443	1448	1661	1817	2975	2978	3001	3002
				3136	3157												
2,4-C_5H_4OH	0.280	0.122	0.085	259	392	439	536	625	640	659	686	712	817	859	919	1004	1030
				1079	1109	1275	1306	1341	1422	1538	1547	3161	3172	3184	3203	3657	
2,4-C_5H_5O[b]	0.245	0.132	0.094	176	397	523	626	690	766	798	804	878	947	968	968	1055	1066
				1090	1118	1276	1311	1363	1574	1603	1871	2843	3030	3038	3062	3068	
1,3-C_5H_5O	0.267	0.123	0.085	178	378	447	536	628	637	764	773	815	922	94	950	1052	1089
				1120	1163	1254	1299	1396	1430	1461	1698	2989	3019	3151	3172	3188	
1,2-C_5H_5O	0.269	0.121	0.085	206	335	444	536	637	655	747	753	870	918	920	962	973	1090
				1118	1180	1278	1319	1348	1441	1612	1628	2951	2967	3152	3183	3185	
C_5H_4O	0.272	0.131	0.088	209	448	449	640	645	714	729	830	839	943	945	949	1084	1087
				1123	1293	1342	1571	1643	1782	3161	3171	3204	3206				
C_5H_4O[b]	0.274	0.131	0.088	194	418	445	620	641	697	729	787	847	864	897	963	1084	1084
				1147	1295	1342	1539	1605	1708	3151	3160	3191	3192				
bicyclo-C_5H_4O	0.333	0.109	0.097	120	388	535	547	660	762	791	839	853	882	960	1001	1025	1034
				1129	1167	1202	1294	1585	1883	3129	3138	3144	3169				
bicyclo-C_5H_4O[b]	0.324	0.110	0.098	122	383	536	551	665	767	783	838	843	884	970	1007	1030	1039
				1127	1165	1201	1296	1529	1831	3129	3139	3139	3160				
C_5H_4 ($^3B_1$)	0.352	0.278	0.155	495	533	587	650	704	804	847	867	926	981	1043	1110	1122	1250
				1358	1439	1477	3153	3166	3207	3210							
C_5H_4 ($^1A_2$)	0.376	0.270	0.161	279	513	592	599	727	775	837	879	953	1026	1078	1095	1214	1257
				1342	1392	1496	3112	3154	3211	3221							

[a] B3LYP/6-31G(d) frequencies multiplied by a scaling factor of 0.98.[15] [b] MP2(full)/6-31G(d) rotational constants and vibrational frequencies. The MP2 frequencies are multiplied by a scaling factor of 0.9646.[24]

enone (C_5H_4O, **12**) thermal decomposition, leading to smaller noncyclic fragments. Emdee et al.[2] proposed that the thermal decomposition of **12** leads to CO + $2C_2H_2$ with the rate expression of k (s^{-1}) = 1×10^{15} exp[−78(kcal/mol)/RT]. In this section, we shall examine the kinetics of C_5H_4O decomposition in greater detail.

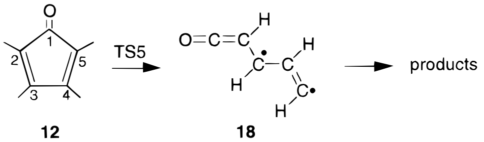
Recognizing the possibilities of multichannel dissociation of **12**, we considered several reaction paths. The first channel is characterized by several isomerization steps, which lead to cyclobutadiene (c-C_4H_4, **17**), as depicted below.



(Channel 1)

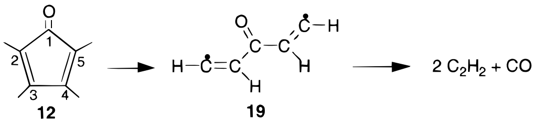
Cyclobutadiene, a molecule rectangular in shape and well-studied for its antiaromaticity,[45,46] is more favorable than the ·HC═CH−CH═CH· biradical, because the $\Delta_fH°_{298}$ of c-C_4H_4 (**17**) is 102 kcal/mol,[47] which is substantially lower than the $\Delta_fH°_{298}$ of the biradical at 147 kcal/mol.[48] The reaction path depicted above involves the isomerization of **12** to the oxobicyclopentene (**13**), which then either directly dissociates to cyclobutadiene (**17**) + CO or isomerizes to the c-C_4H_4CO (**16**) biradical. The elimination of CO from **16** again leads to cyclobutadiene and CO. We note that the cyclobutadiene initially formed from the dissociation of **16** is in the triplet $^3B_1$ state, which lies only 6.9 kcal/mol above that of the ground-state c-C_4H_4 (**17**).[46b]

The second channel breaks the C(1)−C(5) bond in **12**. This step produces the noncyclic •CHCHC•HCHCO biradical (**18**), as shown below. The biradical may then dissociate or isomerize to various products, which are to be discussed later.



(Channel 2)

The third channel involves the breaking of the C(3)−C(4) bond in **12**, leading to the •CHCHCOCHCH• biradical (**19**), which may readily dissociate to form $2C_2H_2$ + CO, i.e.,



(Channel 3)

TABLE 6: Total Energies (Hartrees) and Relative Energies (kcal/mol) Calculated with the G2(MP2,SVP) and G2(B3LYP/MP2,SVP) Method

structure	point group	total energy G2(MP2,SVP)[a]	total energy G2(B3LYP/MP2,SVP)	relative energy[b]
12	C_{2v}	−267.648 32	−267.648 55	0.0
TS1	C_s	−267.545 65		64.4
13	C_s	−267.567 67	−267.568 49	50.6 (50.2)
TS2	C_1	−267.519 15		81.0
TS4	C_s	−267.511 84		85.6
16	C_1	−267.521 27	−267.523 56	79.7 (78.4)
TS3	C_1	−267.506 91	−267.509 65	88.7 (87.1)
17 (+ CO)		−267.554 51	−267.554 39	58.8 (59.1)
TS5	C_1	−267.519 99		80.5
18	C_s	−267.524 85[c]		78.4
$^{\bullet}HC{=}CH{-}CH{=}CH^{\bullet}$ + CO		−267.478 30		106.6
19	C_{2v}	−267.471 99		110.6

[a] Zero-point energies are obtained from the MP2(full)/6-31G(d) geometries with the vibrational frequencies scaled by 0.9646.[24] Hence, these G2(MP2,SVP) energies differ slightly from those listed in Table 3, which are based on the HF zero-point energies. [b] The values in the parentheses are calculated from G2(B3LYP/MP2,SVP) energies. [c] See ref 50.

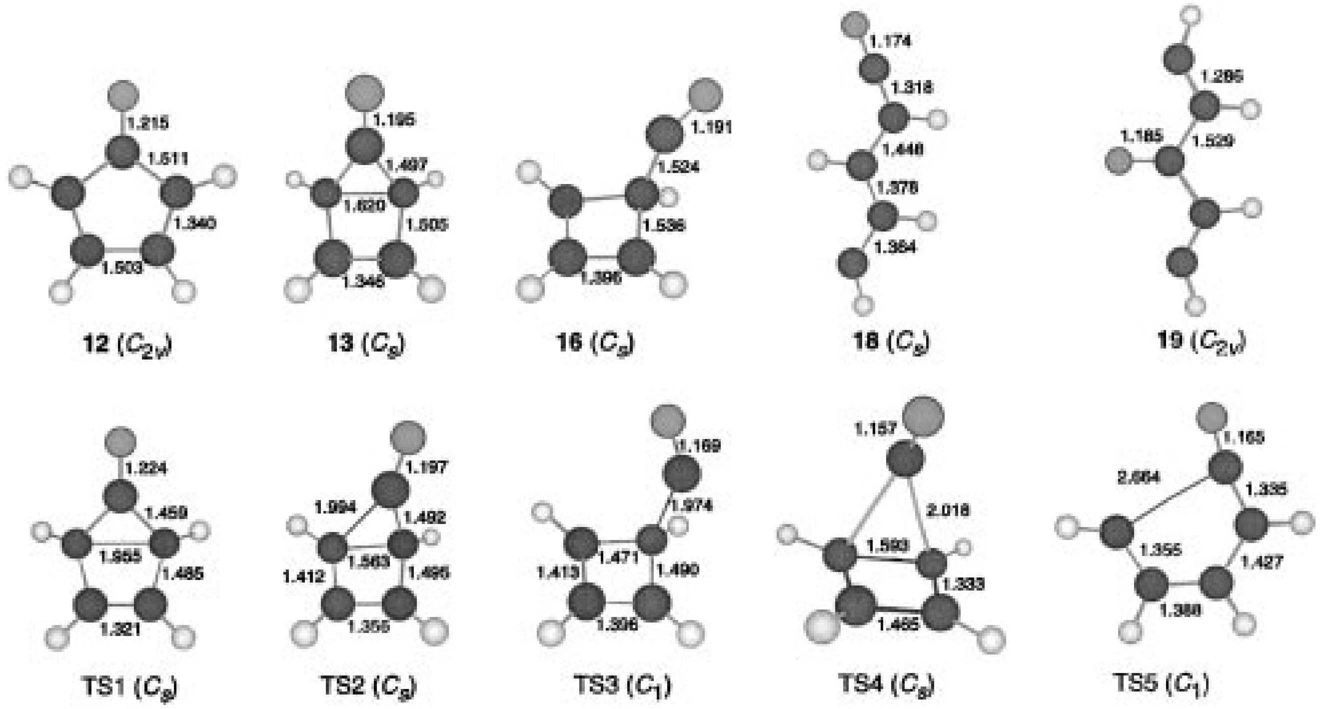


Figure 3. Geometries of the relevant species and transition states of cyclopentadienone thermal decomposition, determined at the MP2(full)/6-31G(d) level of theory.

Table 6 summarizes the total G2(MP2,SVP) energies of the stationary structures and transition states. The energies relative to that of **12** are also presented in the same table. Figure 3 shows the geometries of the stationary points and selected transition states obtained with the MP2(full)/6-31G(d) method. The G2(B3LYP/MP2,SVP) method was also employed for selected species. The results are also shown in Table 6 for comparison. Again, the agreement between the G2(MP2,SVP) and G2(B3LYP/MP2,SVP) energies is very good for both stationary geometries and transition states.

The results in Table 6 show that channel 3 can be readily disregarded because of the high energy associated with the biradical **19**. The minimum energy path of channel 1 was found to be the direct elimination of CO from **13** (TS4). The energy of TS4 is 85.6 kcal/mol above that of **12**. The second biradical route, however, cannot be disregarded because the energy of TS3 is only 3.1 kcal/mol higher than that of TS4. In addition, TS3 represents a loose transition state. Its *A* factor must be larger than that through TS4.

The breaking of the C(1) and C(2) bond in C_5H_4O (**12**) to produce **18** (channel 2) has an energy barrier of 80.5 kcal/mol (TS5), which is comparable with that of channel 1. But the back reaction (**18** → **12**) has such a small energy barrier (2.1 kcal/mol) that unless there is energetically favored exit channels for **18**, channel 2 would remain ineffective. This turns out to be highly likely. We had performed an exhaustive search on the potential energy surface to determine a suitable dissociative or isomerization path of **18**, but found none to be energetically viable. The considered products include C_2H_2 + $H\dot{C}{=}CH{-}\dot{C}{=}O$ or cyclopropenone, propargyl + ketyl, $H\ddot{C}{-}CH{=}CH{-}CH{=}C{=}O$,[50] and ketylcyclopropene. Hence, channel 2 was also excluded from the RRKM calculations.

RRKM Rate Coefficients of Cyclopentadienone Decomposition. The pressure-dependent rate coefficients of cyclopentadienone decomposition following channel 1 were calculated with the RRKM theory.[19] Details of the RRKM code can be found elsewhere.[51] The energy barriers are presented in Figure 4, and the RRKM parameters, in Table 7.

TABLE 7: RRKM Parameters of Cyclopentadienone Thermal Decomposition Following Channel 1, Calculated at the MP2(full)/6-31G(d) Level

12	ν,[a] cm^{-1}	194	418	445	620	641	697	728	787	847	864	897
		963	1084	1085	1147	1295	1343	1539	1605	1709	3152	3161
		3191	3193									
	B_0,[b] cm^{-1}	0.107 (1,2) external inactive; 0.274 (2,1) external active										
	L-J params.[c]	$\sigma = 5.1$Å; $\epsilon/k_B = 484$ K										
13	ν,[a] cm^{-1}	122	383	535	550	665	767	783	838	843	883	970
		1007	1030	1039	1127	1165	1200	1296	1529	1831	3129	3139
		3139	3160									
	B_0,[b] cm^{-1}	0.104 (1,2) external inactive; 0.324 (1,1) external active										
16[d]	ν,[a] cm^{-1}	49	174	418	421	477	574	598	889	906	913	955
		997	997	1152	1180	1202	1272	1299	1489	1864	3010	3162
		3194	3205									
	B_0,[b] cm^{-1}	0.080 (1,2) external inactive; 0.394 (1,1) external active										
TS1	ν,[a] cm^{-1}	951i	239	430	467	595	682	757	767	819	944	964
		995	1033	1104	1119	1233	1272	1346	1530	1734	3145	3146
		3169	3190									
	B_0,[b] cm^{-1}	0.100 (1,2) external iinactive; 0.341 (1,1) external active										
TS2[d]	ν,[a] cm^{-1}	656i	106	337	444	508	605	764	828	869	923	962
		989	1011	1112	1153	1193	1205	1324	1525	1836	3053	3159
		3185	3203									
	B_0,[b] cm^{-1}	0.090 (1,2) external inactive; 0.363 (1,1) external active										
TS3	ν,[a] cm^{-1}	630i	50[e]	142	171	332	490	531	598	776	815	874
		912	924	991	1118	1198	1233	1313	1402	1892	3116	3171
		3199	3210									
	B_0,[b] cm^{-1}	0.077 (1,2) external inactive; 0.330 (1,1) external active 1.12 (1,1) internal active										
TS4	ν,[a] cm^{-1}	683i	165	178	309	493	620	664	804	839	872	919
		949	1051	1062	1134	1189	1278	1374	1620	2015	3154	3170
		3213	3217									
	B_0,[b] cm^{-1}	0.098 (1,2) external inactive; 0.257 (1,1) external active										

[a] Based on MP2(full)/6-31G(d) frequencies scaled by 0.9646.[24] [b] The numbers in parentheses are the symmetry number and the dimension of the rotor, in that order. [c] Reference 2. [d] Not used in the actual RRKM calculation (see text). [e] The vibrational motion is replaced by an internal free rotor,[19b] and the frequency is not used in the RRKM calculation.

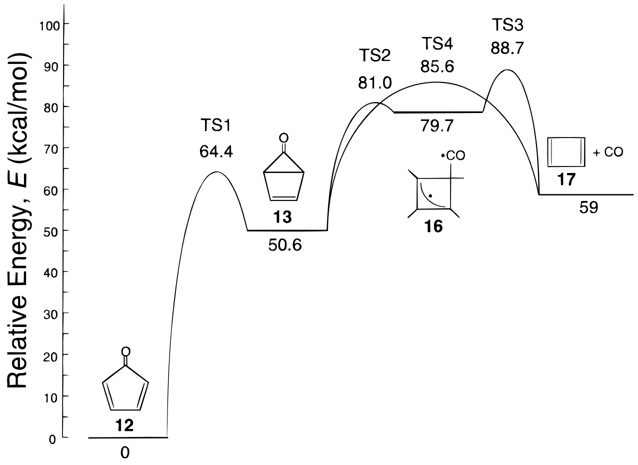
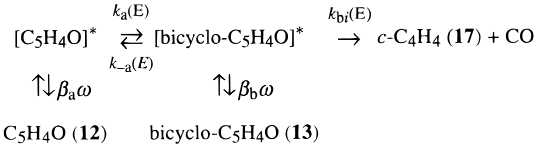


Figure 4. Energy diagram of cyclopentadienone thermal decomposition.

To simplify the RRKM calculations, **16** was not considered as a stationary point, because it represents basically a shallow well on the potential energy surface. The collisional stabilization of **16** is expected to be inefficient. Hence, excluding it from the RRKM treatment has only negligible effects on the rate coefficient prediction.

The following reaction scheme was considered.



$$\begin{array}{ccccc} [C_5H_4O]^* & \underset{k_{-a}(E)}{\overset{k_a(E)}{\rightleftarrows}} & [\text{bicyclo-}C_5H_4O]^* & \xrightarrow{k_{bi}(E)} & c\text{-}C_4H_4\ (\mathbf{17}) + CO \\ \uparrow\downarrow\beta_a\omega & & \uparrow\downarrow\beta_b\omega & & \\ C_5H_4O\ (\mathbf{12}) & & \text{bicyclo-}C_5H_4O\ (\mathbf{13}) & & \end{array}$$

where $k(E)$ are the microcanonical rate constant, and $i = 1$ and 2 denote the fluxes through the transition states TS3 and TS4, respectively. Assuming $[C_5H_4O]^*$ and $[\text{bicyclo-}C_5H_4O]^*$ are in the steady state, we obtain the thermal rate coefficients for

$$C_5H_4O\ (\mathbf{12}) \xrightarrow{k_1} \text{bicyclo-}C_5H_4O\ (\mathbf{13}) \tag{1}$$

$$C_5H_4O\ (\mathbf{12}) \xrightarrow{k_{2i}} c\text{-}C_4H_4\ (\mathbf{17}) + CO \tag{2}$$

$$\text{bicyclo-}C_5H_4O\ (\mathbf{13}) \xrightarrow{k_{3i}} c\text{-}C_4H_4\ (\mathbf{17}) + CO \tag{3}$$

as

$$k_1 = \int_0^\infty \frac{k_a(E)\, P_a(E)}{Z(E)}\, dE \tag{4}$$

$$k_{2,1} = \int_0^\infty \frac{k_a(E)\, k_{b1}(E)\, P_a(E)}{\beta_b \omega Z(E)}\, dE \tag{5a}$$

$$k_{2,2} = \int_0^\infty \frac{k_a(E)\, k_{b2}(E)\, P_a(E)}{\beta_b \omega Z(E)}\, dE \tag{5b}$$

$$k_{3,1} = \int_0^\infty \frac{[\beta_a\omega + k_a(E)] k_{b1}(E)\, P_b(E)}{\beta_a \omega Z(E)}\, dE \tag{6a}$$

$$k_{3,2} = \int_0^\infty \frac{[\beta_a\omega + k_a(E)] k_{b2}(E)\, P_b(E)}{\beta_a \omega Z(E)}\, dE \tag{6b}$$

where $P_a(E)$ and $P_b(E)$ are respectively the Boltzmann distribution functions of **12** and **13**, ω is the collision frequency, β is the collision efficiency factor calculated with eq 4.7 of ref 52,

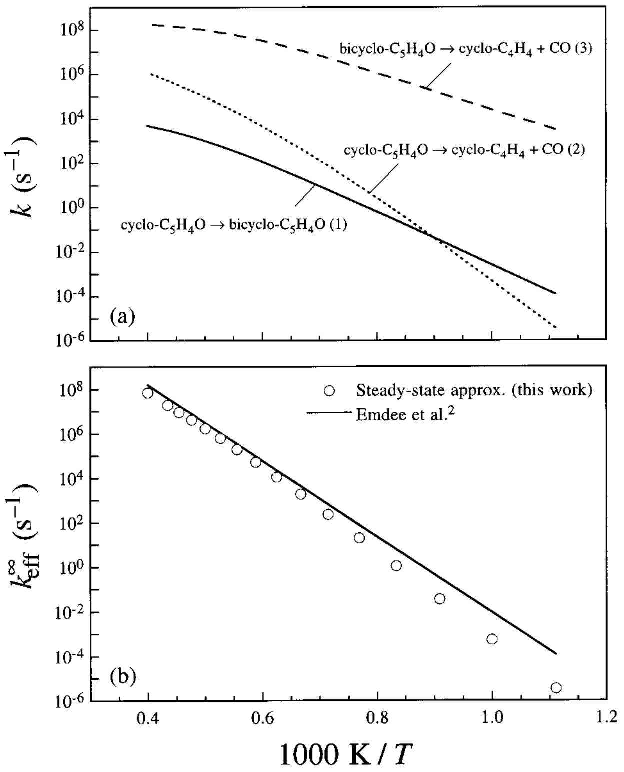


Figure 5. Rate coefficients computed for cyclopentadienone thermal decomposition (a) at a pressure of 1 atm with N_2 as the third body ($\langle E_{\mathrm{down}} \rangle = 260$ cm^{-1}), and (b) comparison of the present high-pressure limit rate coefficient with the bicyclo-C_5H_4O in the steady state (eq 7) and the thermochemical estimate of Emdee et al.[2]

which considers a high-temperature nonequilibrium factor in the approximation of β, and

$$Z(E) = 1 + \frac{k_a(E)}{\beta_a\omega} + \frac{k_{-a}(E) + [k_{b1}(E) + k_{b2}(E)][1 + k_a(E)/\beta_a\omega]}{\beta_b\omega}$$

The total thermal rate coefficients of reactions 2 and 3 are equal to the sum of the fluxes through TS3 and TS4, respectively, and thus $k_{2(\mathrm{tot})} = k_{2,1} + k_{2,2}$, and $k_{3(\mathrm{tot})} = k_{3,1} + k_{3,2}$. The pressure falloff rate coefficients were computed with N_2 as the third body, and an average energy transfer per down collision $\langle E_{\mathrm{down}} \rangle = 260$ cm^{-1}. The high-pressure limit rate coefficients can be readily derived with eqs 4-6 modified in accordance with the conditions of $\omega \rightarrow \infty$. They are

$$k_1^{\infty} = \int_0^{\infty} k_a(E)\, P_a(E)\, dE \qquad (7)$$

$$k_{2,i}^{\infty} = \int_0^{\infty} \frac{k_a(E)\, k_{bi}(E)\, P_a(E)}{\beta_b\omega} \qquad (8)$$

$$k_{3,i}^{\infty} = \int_0^{\infty} k_{bi}(E)\, P_b(E)\, dE \qquad (9)$$

Figure 5a presents the rate coefficients computed at a pressure of 1 atm. It is seen that reaction 17 dominates the overall thermal decomposition of C_5H_4O (**12**) for temperatures above 1250 K. However, the isomerization of **12** to **13** is seen to dominate below 1250 K.

We note that the asymptotic behavior of eq 5 at high pressures is that k_2 becomes inversely proportional to pressure and is equal to zero at the high-pressure limit. Hence, to compare the present results with the thermochemical estimate of Emdee et al.,[2] we used the high-pressure limit rate coefficients of reactions 1 and 3. It is assumed that the bicyclo-C_5H_4O (**13**) in the following reaction sequence,

$$C_5H_4O\ (\mathbf{12}) \underset{k_{-1}^{\infty}}{\overset{k_1^{\infty}}{\rightleftharpoons}} \text{bicyclo-}C_5H_4O\ (\mathbf{13}) \xrightarrow{k_3^{\infty}} c\text{-}C_4H_4\ (\mathbf{17}) + CO$$

can be treated by the steady-state assumption. It follows that the effective rate coefficient for the thermal decomposition of **12**,

$$C_5H_4O\ (\mathbf{12}) \xrightarrow{k_{\mathrm{eff}}^{\infty}} c\text{-}C_4H_4\ (\mathbf{17}) + CO$$

is

$$k_{\mathrm{eff}}^{\infty} = \frac{k_1^{\infty} k_3^{\infty}}{k_{-1}^{\infty} + k_3^{\infty}} \qquad (10)$$

Figure 5b presents the comparison between $k_{\mathrm{eff}}^{\infty}$ and the rate coefficient estimate of Emdee et al.[2] It is seen that despite the large difference in the activation energy adopted by Emdee et al.[2] (78 kcal/mol) and the energy barrier determined in the present study (~90 kcal/mol), the agreement in the rate coefficients is surprisingly good. The reason is that in eq 7 $k_{-1}^{\infty} >> k_3^{\infty}$, and thus $k_{\mathrm{eff}}^{\infty} \cong (k_1^{\infty}/k_{-1}^{\infty})k_3^{\infty}$. Because the A factor of $k_{3,1}^{\infty}$ is quite large ($A_{3,1}^{\infty} = 1.3 \times 10^{16}$ s^{-1}) because of a loose transition state (TS3), the A factor in $k_{\mathrm{eff}}^{\infty}$ is larger than that estimated by Emdee et al.[2]

Despite the reasonably good agreement in the rate coefficients at the high-pressure limit, we recommend that the thermal decomposition kinetics of cyclopentadienone should be modeled by including reactions 1−3 and taking into consideration the appropriate pressure falloff effects. The Arrhenius rate parameters are fitted to the RRKM results and are tabulated in Table 8 at several representative pressures.[53]

Thermal Decomposition of Cyclobutadiene. The noncyclic species are probably produced from the subsequent c-C_4H_4 dissociation. It was suggested[54] that the linearization of c-C_4H_4 to $^{\bullet}HC{=}CH{-}CH{=}CH^{\bullet}$ has an energy barrier of 42 kcal/mol,[46e] and the biradical decomposition to $C_2H_2 + C_2H_2$ has an energy barrier of 9 kcal/mol. Hence, the overall energy barrier of

$$c\text{-}C_4H_4 \rightarrow C_2H_2 + C_2H_2$$

can be estimated to be 51 kcal/mol. In addition, the thermally energized biradical may undergo 2,3-H_2 elimination to form diacetylene and H_2, or it may isomerize to vinylacetylene, i.e.,

$$c\text{-}C_4H_4 \rightarrow C_4H_2 + H_2$$

$$c\text{-}C_4H_4 \rightarrow HC{\equiv}C{-}CH{=}CH_2$$

but both should have higher energy barriers, at 56 and 64 kcal/mol,[46e] than decomposition to two C_2H_2.

In addition to the reaction channels just discussed, we note that there exist numerous isomers that lie in the energy range 0−50 kcal/mol above the energy of cyclobutadiene. This offers possibilities of additional reaction channels that may lead to the thermal dissociation of cyclobutadiene. One such possible channel involves a 1,2-H shift in c-C_4H_4, followed by isomerization to methylenecyclopropene, which then dissociates to acetylene and vinylidene.

TABLE 8: RRKM Rate Coefficient Parameters[a] for the Cyclopentadienone Thermal Decomposition Reaction

		$k = AT^n \exp(-E/RT)$ [M]			
	P (atm)	A	n	E	comments
k_1					
	0.1	7.0×10^{31}	−6.88	66.9	
	1	5.7×10^{32}	−6.76	68.5	
	10	4.4×10^{31}	−6.06	69.5	
	100	2.9×10^{27}	−4.50	69.1	
	∞	3.0×10^{13}		65.1	
$k_{2,1}$	0.1	2.7×10^{49}	−10.31	101.2	
	1	5.0×10^{43}	−8.41	100.1	
	10	2.1×10^{35}	−5.81	97.3	
	100	5.8×10^{32}	−4.92	97.7	
$k_{2,2}$	0.1	2.7×10^{44}	−9.40	96.8	
	1	1.3×10^{39}	−7.65	95.7	
	10	1.0×10^{32}	−5.43	93.4	
	100	1.1×10^{30}	−4.74	94.2	
$k_{2(\text{tot})}$	0.1	1.1×10^{47}	−9.63	99.5	
	1	6.2×10^{41}	−7.87	98.7	
	10	1.8×10^{33}	−5.22	95.8	
	100	7.3×10^{30}	−4.39	96.3	
$k_{3,1}$	0	7.9×10^{44}	−8.18	40.4	$k_{3,1}$/[M]
	0.1	4.3×10^{55}	−12.55	65.3	*b*
	1	6.9×10^{43}	−9.00	56.6	*b*
	10	1.1×10^{37}	−6.89	50.5	*b*
	100	3.1×10^{37}	−6.77	49.9	*b*
	∞	1.3×10^{16}		39.9	
$k_{3,2}$	0	9.9×10^{56}	−12.14	40.5	$k_{3,2}$/[M]
	0.1	1.5×10^{53}	−12.40	62.2	*b*
	1	3.4×10^{39}	−8.37	51.6	*b*
	10	6.5×10^{33}	−6.57	46.0	*b*
	100	1.1×10^{35}	−6.67	46.0	*b*
	∞	8.1×10^{13}		36.3	
$k_{3(\text{tot})}$	0	8.4×10^{43}	−8.00	36.4	$k_{3(\text{tot})}$/[M]
	0.1	4.3×10^{55}	−12.55	65.3	*b*
	1	6.9×10^{43}	−9.00	56.6	*b*
	10	1.1×10^{37}	−6.89	50.5	*b*
	100	3.1×10^{37}	−6.77	49.9	*b*
	∞	1.6×10^{13}	0.824	38.0	

[a] Units in cm, s, mol, kcal, and K. Unless otherwise indicated, the rate parameters are fitted within the temperature range 300−2500 K. [b] Fitted for the temperature range 800−2500 K.

Singlet Cyclopentadienylidene as an Intermediate Species? For the two cyclopentadienylidene radicals (**14, 15**), we found that the enthalpy difference between the singlet $^1A_2$ state and the ground triplet $^3B_1$ state to be 6.4 kcal/mol, in close agreement with the earlier theoretical results of 7.3 kcal/mol[55] and 6.3 kcal/mol,[56] and the experimental result of 5.8 kcal/mol, based on the measurements of electron photodetachment (EPD) thresholds of the c-$C_5H_4^-$ anion radical.[38] On the absolute scale, however, the predicted $\Delta_fH°_{298}$ (**14**) = 125.2 kcal/mol and $\Delta_fH°_{298}$ (**15**) = 131.6.1 kcal/mol are significantly larger than the respective experimental data[38] at 112.3 ± 4.7 and 118.1 ± 4.7 kcal/mol. Because of the critical importance of the thermochemistry of the cyclopentadienylidene radicals in interpreting the oxidation mechanism of cyclopentadiene, as will be discussed later, the discrepancies between the experimental and theoretical $\Delta_fH°_{298}$ values warrant further discussion.

We first consider the accuracy of the theoretical methods employed for energy prediction for strained singlet radial species, such as the cyclopropenylidene, c-C_3H_2 ($^1A_1$). At the G2(B3LYP/MP2,SVP) level, we computed the total energy of c-C_3H_2 to be −115.137 60 hartrees. The $\Delta_fH°_{298}$ value of c-C_3H_2 can be estimated from its atomization energy with the total energies of C and H taken from Table 1. Using the respective $\Delta_fH°_{298}$ values of 52.1 and 142.2 kcal/mol for H and C,[25] we obtained $\Delta_fH°_{298}$ = 118 kcal/mol for c-C_3H_2 ($^1A_1$), in excellent agreement with the recent experimental data of 119.5 ± 2.2 kcal/mol.[57]

The experimental results of **14** and **15** were obtained as the sum of the electron affinities (EA), determined by the thresholds of EPD from the c-$C_5H_4^-$ anion radical,[38] and the $\Delta_fH°_{298}$ of c-$C_5H_4^-$, determined with the ion/molecule reaction bracketing (IMRB) technique.[38,39] The experimental EA values are 40.4 ± 1.1 kcal/mol for **14** and 46.2 ± 0.2 kcal/mol for **15**. The experimental $\Delta_fH°_{298}$(c-$C_5H_4^-$) is 71.9 ± 3.6 kcal/mol.

We next examine the computed EA values. Calculations at the G2(B3LYP/MP2,SVP) level yielded the total energy of c-$C_5H_4^-$ equal to −192.460 57 hartrees. Then, the computed electron affinity of **14** is E(**14**) − E(c-$C_5H_4^-$) = 42.7 kcal/mol, and of **15**, E(**15**) − E(c-$C_5H_4^-$) = 46.0 kcal/mol. These values are in close agreement with the experimental results of ref 38. Hence, the disagreement between the theoretical and experimental $\Delta_fH°_{298}$ values of **14** and **15** must come from the discrepancy in the c-$C_5H_4^-$ anion.

Indeed, the $\Delta_fH°_{298}$ of c-$C_5H_4^-$ determined from the G2(B3LYP/MP2,SVP) atomization energy yielded $\Delta_fH°_{298}$ (c-$C_5H_4^-$) = 83 kcal/mol, which is larger than the experimental counterpart by about 11 kcal/mol. Hence, either the experimental $\Delta_fH°_{298}$ value of the c-$C_5H_4^-$ anion is in error, or the present theoretical values for the anion radical and the triplet and singlet c-C_5H_4 radicals are all too high by 11−13 kcal/mol. The latter is highly unlikely considering the error limits of the theoretical methods and the close prediction for the cyclopropenylidene radical discussed previously.

To further substantiate the above discussion, we computed the G2(B3LYP/MP2,SVP) energy for the cyclopentadienyl anion (c-$C_5H_5^-$) and obtained E_0 = −193.142 35 hartrees, which can be used to compute the ionization energy of $C_5H_5^-$ (c-$C_5H_5^- \rightarrow C_5H_5$(**2**) + e). Using $\Delta_fH°_{298}$ = 62 kcal/mol for C_5H_5, we obtained $\Delta_fH°_{298}$ = 17.8 kcal/mol, which is in excellent agreement with the experimental data of 19.6 ± 3.8 kcal/mol of ref 58 and 18.9 ± 1.9 kcal/mol of ref 59. On the basis of the above discussion, we found that there is no reason to think that our $\Delta_fH°_{298}$ values for the cyclopentadienylidene are inaccurate. Furthermore, we note that the problems associated with IMRB have been well-documented when the technique is used for the determination of thermochemistry.[60]

We next examine the possibility of the singlet cyclopentadienylidene as an intermediate species during the oxidation of cyclopentadiene. The importance of c-C_5H_4 ($^1A_2$) can be appreciated by the fact that it may be able to react with molecular oxygen without an appreciable energy barrier. Such a reaction would provide secondary chain branching and presumably leads to ring breakdown. Hence, if the production of c-C_5H_4 is substantial, it is necessary to consider the relevant reaction channels leading to its formation and destruction.

The singlet cyclopentadienylidene may be produced from the chemically activated reactions of C_5H_5 (**2**) with H, O, OH, HO_2, and O_2, as shown in Figure 6. These are chemically activated radical−radical combinations, followed by dissociation of the hot adducts to C_5H_4 ($^1A_2$). For comparison, the reaction channels leading to products other than C_5H_4 ($^1A_2$) are included in the same figure. Because the radical−radical combination reactions and the insertion of the singlet c-C_5H_4 into H_2, OH, H_2O, H_2O_2, and HO_2 are expected to proceed without an appreciable energy barrier, an examination of the reaction enthalpy is sufficient to determine the relative importance of certain reaction channels. For a preliminary screening, the energy barriers of several isomerization steps have been

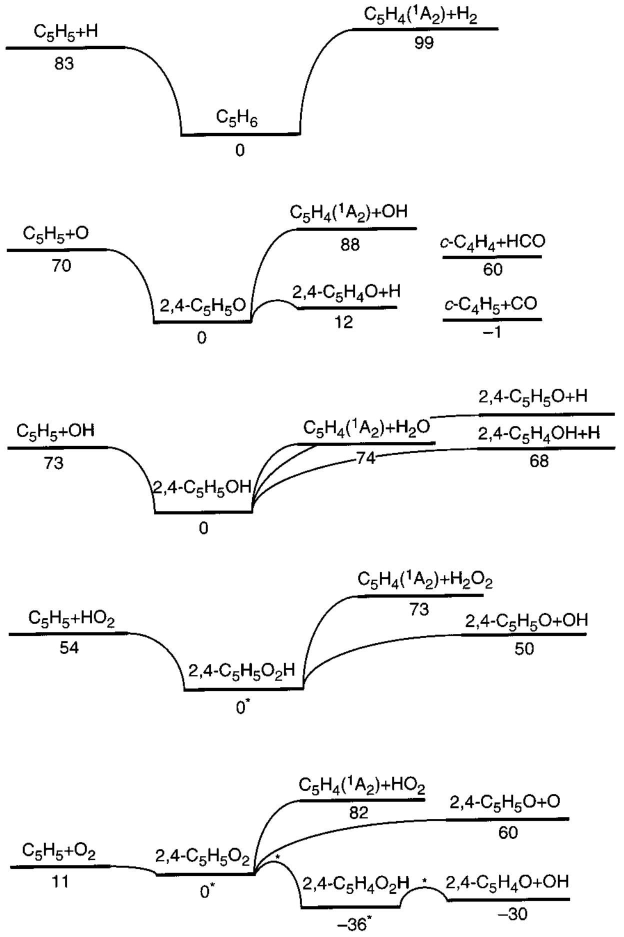


Figure 6. Energy diagram of the reactions of the cyclopentadienyl radical with H, O, OH, HO_2, and O_2. The asterisks indicate that the energy levels were computed with the semiempirical PM3 method.[61]

estimated with the semiempirical PM3 method.[61] These energies are marked by the asterisks in Figure 6.

It is seen that only the reaction

$$C_5H_5 + OH \rightarrow C_5H_4\ (^1A_2) + H_2O$$

is feasible for appreciable C_5H_4 ($^1A_2$) production, but even this reaction is only thermally neutral and suffers competition from

$$C_5H_5 + OH \rightarrow 2{,}4\text{-}C_5H_4OH + H$$

All other reactions producing C_5H_4 ($^1A_2$) are significantly endothermic. With the presence of energetically favored channels leading to the dissociation of the respective hot adducts, we expect limited C_5H_4 ($^1A_2$) production from the reactions of C_5H_5 with O, HO_2, and O_2. On the basis of the above discussion, the C_5H_4 ($^1A_2$) chemistry is not expected to be significant during cyclopentadiene oxidation at low to intermediate temperatures, but it may well contribute to the overall oxidation at high temperatures. We note that if we adopt the lower $\Delta_f H^\circ_{298}$ value of ref 38 for C_5H_4 ($^1A_2$), its production would be competitive over a wide range of temperatures. But this is unlikely for reasons already discussed.

IV. Summary

The enthalpies of formation of 15 intermediate species of cyclopentadiene oxidation were determined by molecular orbital calculations at the G2(MP2,SVP) and G2(B3LYP/MP2,SVP) levels of theory. The G2(B3LYP/MP2,SVP) method was devised in the present study and was shown to provide atomization energies with accuracy comparable with G2(MP2) and G2(B3LYP/MP2). The thermal decomposition kinetics of cyclopentadienone was examined. It is concluded that the decomposition of cyclopentadienone leads primarily to cyclobutadiene. The pressure-dependent rate coefficients were computed with the RRKM theory and reported for future kinetic modeling studies. On the basis of the presently determined enthalpies of formation, the production of the singlet cyclopentadienylidene is seen to be feasible at high temperatures through the reaction between the cyclopentadienyl and OH radicals, which may need to be taken into consideration in the kinetic model of aromatics combustion.

Acknowledgment. The work utilized the computer system Power Challenge Array at the National Center for Supercomputing Applications, University of Illinois at Urbana—Champaign. We thank Prof. Alexander Burcat, Dr. Kerwin D. Dobbs, and Prof. Douglas J. Doren for helpful discussions.

References and Notes

(1) Brezinsky, K. *Prog. Energy Combust. Sci.* **1986**, *3*, 1.

(2) Emdee, J. L.; Brezinsky, K.; Glassman, I. *J. Phys. Chem.* **1992**, *96*, 2151.

(3) Lindstedt, R. P.; Skevis, G., *Combust. Flame* **1994**, *99*, 551.

(4) Zhang, H.-Y.; McKinnon, J. T. *Combust. Sci. Technol.* **1995**, *107*, 261.

(5) Tan, Y. W.; Frank, P. *Twenty-Sixth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, in press.

(6) Bittner, J. D.; Howard, J. B. *Eighteenth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1980; p 1105.

(7) Davis, S. G.; Wang, H.; Brezinsky, I.; Law, C. K. *Twenty-Sixth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, in press.

(8) Lindstedt, R. P.; Maurice, L. Q. *Combust. Sci. Technol.* **1996**, *120*, 119.

(9) Karni, M.; Oref, I.; Burcat, A. *J. Phys. Chem. Ref. Data* **1991**, *20*, 665.

(10) Disch, R. L.; Schulman, J. M.; Sabio, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1904.

(11) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem Phys.* **1991**, *94*, 7221.

(12) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem Phys.* **1993**, *98*, 1293.

(13) Smith, B. J.; Radom, L. *J. Phys. Chem.* **1995**, *99*, 6468. Curtiss, L. A.; Redfern, P. C.; Smith, B. J.; Radom, L. *J. Chem Phys.* **1996**, *104*, 5148.

(14) Mebel, A. M.; Morokuma; Lin, M. C. *J. Chem. Phys.* **1995**, *103*, 7414.

(15) Bauschlicher, C. W., Jr.; Partridge, H. *J. Chem. Phys.* **1995**, *103*, 1788.

(16) Glukhovtsev, M. N.; Laiter, S.; Pross, A. *J. Phys. Chem.* **1995**, *99*, 6828.

(17) Glukhovtsev, M. N.; Bach, R. D.; Laiter, S. *J. Phys. Chem.* **1996**, *100*, 10952.

(18) Wang, H.; Law, C. K. *J. Phys. Chem.* **1997**, *101*, 3400.

(19) See, for example: (a) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley: New York, 1972. (b) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Scientific: Oxford, 1990.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision D.4; Gaussian, Inc.: Pittsburgh, PA, 1995.

(21) Stevens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(22) Hehre, W. J.; Ditchfield, R.; Radom, L.; Pople, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 4796.

(23) Peng, C.; Schlegal, H. B. *Isr. J. Chem.* **1993**, *33*, 449.

(24) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345.

(25) *JANAF Thermochemical Tables*; Natl. Stand. Ref. Data Ser.; U.S. Natl. Bur. Stand., 1985; Vol 37.

(26) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: London, 1986.

(27) Tsang, W. In *Energetics of Organic Free Radicals*; Martinho Simoes, J.A., Greenberg, A., Liebman, J. F., Eds.; Blackie Academic and Professional: London, 1996; pp 22−58.

(28) Ruscic, B.; Berkowitz, J. *J. Chem. Phys.* **1994**, *101*, 10936.

(29) Holmes, J. L.; Lossing, F. P.; Meyer, P. M. *J. Am. Chem. Soc.* **1991**, *113*, 9723.

(30) Curtiss, L. A.; Lucas, D. J.; Pople, J. A. *J. Chem. Phys*. **1985**, *102*, 3292, and references therein.

(31) Holmes, J. L.; Lossing, F. P. *J. Am. Chem. Soc.* **1982**, *104*, 2648.

(32) Burcat, A.; McBride, B.; Rabinowitz, M. *1990 Ideal Gas Thermodynamic Data for Compounds Used in Combustion*; Technion Report No. T.A.E. 657; Israel, 1990.

(33) Defrees, D. J.; Mclver, R. T., Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334.

(34) Bartmess, J. E.; Scott, J. A.; McIver, R. T. *J. Am. Chem. Soc.* **1979**, *101*, 6046. Cumming, J. B.; Kebarle, P. *Can. J. Chem. Phys*. **1978**, *56*, 1.

(35) Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* **1977**, *67*, 1412.

(36) Telnoi, V. I.; Rabinovitch, I. B. *Russ. Chem. Rev.* **1977**, *46*, 689.

(37) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. Puttemans, J. P.; Smith, G. P.; Golden, D. M. *J. Phys. Chem.* **1990**, *94*, 3227.

(38) McDonald, R. N.; Bianchina, E. J., Jr.; Tung, C. C. *J. Am. Chem. Soc.* **1991**, *113*, 7115.

(39) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, *6491*.

(40) Jahn, J. A.; Teller, E. *Proc. R. Soc.* **1937**, *161*, 220.

(41) Clark, T.; Chandrasekhar, J.; Schleyer, P. V. R.; Saunders, M. *J. Chem. Soc. Chem. Commun.* **1980**, 265.

(42) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1979**, *101*, 3771.

(43) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

(44) Liebling, G. R.; McConnell, H. M. *J. Chem. Phys.* **1965**, *42*, 3931. Hedaya, E. *Acc. Chem. Res.* **1969**, *2*, 367.

(45) For example: Lewis, D.; Peters, D. *Facts and Theories of Aromaticity*; Macmillan: London, 1975. Bally, T.; Masamune, S. *Tetrahedron* **1980**, *36*, 343. Maier, G. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 309. Arnold, B. R.; Michi, J. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 1. Cram, D. J.; Tanner, M. E.; Thomas, R. *Angew Chem., Int. Ed. Engl.* **1991**, *30*, 1024. Minkin, V. I.; Glukhovtsev, M. N.; Simkin, B. Ya. *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*; Wiley: New York, 1994.

(46) Theoretical studies, see ref 16 and others including: (a) Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 2617. (b) Hess, B. A.; Schaad, L. J. *J. Am. Chem. Soc.* **1985**, *107*, 865. (c) Disch, R. L.; Schulman, J. M.; Sabio, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 1904. (d) Staley, W. W.; Norden, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 445. (e) Zhang, M.-Y.; Wesdemiotis, C.; Marchetti, M.; Danis, P. O.; Ray, J. C.; Carpenter, B. K.; McLafferty, F. W. *J. Am. Chem. Soc.* **1989**, *111*, 8341. (f) Balková, A.; Bartlett, R. J. *J. Chem. Phys.* **1994**, *101*, 8972. (g) Mo, Y.; Wu, W.; Zhang, Q. *J. Phys. Chem.* **1994**, *94*, 10048. (h) Torii, H.; Tasumi, M. *J. Mol. Struct.* **1996**, *376*, 317.

(47) $\Delta_f H^\circ_{298} = 102 \pm 1$ kcal/mol for c-C_4H_4 based on calculations using the G2 method.[16] Our own calculation at the G2(MP2,SVP) level of theory and with the use of the isodesmic reaction $c\text{-}C_4H_4 + 4CH_4 = 2C_2H_6 + 2C_2H_4$ yielded $\Delta_f H^\circ_{298}(c\text{-}C_4H_4) = 102$ kcal/mol, in perfect agreement with the G2 result.

(48) Based on the G2(MP2,SVP) energy of −154.302 59 hartrees for the biradical and the enthalpy of isodesmic reaction $^{\bullet}HC{=}CH{-}CH{=}CH^{\bullet} + 2CH_4 = 2C_2H_3 + C_2H_6$. Note that the group additivity method with $\Delta_f H^\circ_{298} = 26$ kcal/mol for 1,3-butadiene and the vinylic C−H bond dissociation energy of 111 kcal/mol[49] yields a lower $\Delta_f H^\circ_{298}$ for the biradical at 144 kcal/mol.

(49) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750.

(50) The total G2(MP2,SVP) energy of the singlet $\ddot{H}{-}CH{=}CH{-}CH{=}C{=}O$ biradical was found to be about equal to that of the triplet $H\dot{C}{=}CH{-}CH{=}CH{-}\dot{C}{=}O$ radical.

(51) Wang, H.; Frenklach, M. *J. Phys. Chem.* **1994**, *98*, 11465.

(52) Gilbert, R. G.; Luther, K.; Troe, J. *Ber. Bunsen-Ges. Phys. Chem.* **1983**, *87*, 169.

(53) The thermochemical data of the bicyclo-C_5H_4O (**13**), along with all other species shown in Figure 1, can be obtained at the World Wide Web address http://www.me.udel.edu/∼hwang/C_5H_6.thermo.

(54) Kollmar, H.; Carrion, F.; Dewar, M. J. S.; Bingham, R. C. *J. Am. Chem. Soc.* **1981**, *103*, 5292.

(55) Bofill, J. M.; Bru, N.; Farroàs, J.; Olivella, S.; Solé, A.; Vilarrasa, J. *J. Am. Chem. Soc.* **1988**, *110*, 3740.

(56) Collins, C. L.; Davy, R. D.; Schaefer, H. F., III. *Chem. Phys. Lett.* **1990**, *171*, 259.

(57) Chyall, L. J.; Squires, R. R. *Int. J. Mass Spectrom. Ion Processes* **1995**, *149/150*, 257.

(58) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6047.

(59) DiDomenico, A.; Harland, P. W.; Franklin, J. L. *J. Chem. Phys.* **1972**, *56*, 5299.

(60) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *Gas-Phase Ion and Neutral Thermochemistry*; American Institute of Physics: New York, 1988; *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(61) Stewart, J. J. P. *J. Comput. Chem*. **1989**, *10*, 209.