

Figure 4. Comparison of theoretical and experimental data of in-plane ethylenepropellanes (numbering of compounds as in Table I).

In the carbon atom, the normal valence that can be used for covalent bonding is 4. This situation is realized in CH_4 . In this case, the valence reduction ΔV_M is zero. However, for CH_3 the atomic valence number $V_C \approx 3$. The valence change $\Delta V_M \approx 1$. This is typical for a radical. The difference between a diradical and zwitterion in this theory is that $\Delta V_M^{Cl} \approx 2$ and $\Delta V_M^{RHF} \ll$

1 for the former and $\Delta V_M^{RHF} \approx 2$ and $\Delta V_M^{Cl} \ll 1$ for the latter.¹¹

We have now collected energy, dipole moment, and valence data on twelve ethylenepropellanes in Table I. It is easy to observe that there are two groups of compounds. The first group is characterized by small singlet-triplet energy gaps, dipole moments of a few debye, and dominant ΔV_M^{Cl} terms for the valence change. These are classified as diradicals (D). The second group is characterized by large singlet-triplet energy gaps, dipole moments of >10 D, and a dominant ΔV_M^{RHF} valence change. These systems are classified as zwitterions (Z). A closer look reveals that the diradicals are acceptor-substituted ethylenepropellanes and the zwitterions donor-substituted ethylenepropellanes. Experimental observation indicates copolymerization by acceptor-substituted olefins with propellanes and homopolymerization by methoxy-substituted or no polymerization by other donor-substituted olefins. From our calculations, the following prediction emerges from comparison between theoretical and experimental data (Figure 4): We predict that, similar to the situation in tetramethylene, diradicals initiate copolymerization and that zwitterions initiate homopolymerization or no polymerization at all. For the presently known experimental data this agreement is perfect.

Conclusion

A newly introduced criterion for the distinction of diradicals and zwitterions can be successfully used to predict the polymerization mechanism of ethylenepropellanes. Acceptor-substituted ethylenepropellanes are diradicals and initiate copolymerization, whereas donor-substituted ethylenepropellanes are zwitterions and could initiate homopolymerization. [1.1.1]Propellane itself is neither a diradical nor a zwitterion but can be best characterized as a 1,2-dipole. Polymerization of pure [1.1.1]propellane therefore does not seem to proceed initially on the singlet surface but on the triplet surface where diradical properties are prevalent.

Acknowledgment. The calculations were performed on a CYBER 180-995 at Universität Hannover. We thank Fonds der Chemischen Industrie for partial support of this work.

Cyclopentadienylidencarbene: A Stable Isomer of *o*-Benzyne?

Neil A. Burton, Geoffrey E. Quelch, Mary M. Gallo, and Henry F. Schaefer, III*

Contribution No. 115 from the Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602. Received May 24, 1990

Abstract: High-level ab initio quantum-mechanical studies have been performed on cyclopentadienylidencarbene, an experimentally unknown species thought to be an important isomerization product of *o*-benzyne. Results suggest that cyclopentadienylidencarbene is a shallow minimum on the PE surface, being bound by less than 5 kcal mol⁻¹. Harmonic vibrational frequencies have been evaluated at the self-consistent-field (SCF) level, together with the singlet-triplet energy difference, electron affinity, and lowest ionization energy at the configuration interaction (CI) level. The study provides the valuable detail and insight into cyclopentadienylidencarbene necessary for its experimental detection and characterization.

Introduction

Evidence for the existence of cyclopentadienylidencarbene (methylene, 2,4-cyclopentadien-1-ylidene), as an isomerized product of *o*-benzyne (1,3-cyclohexadien-5-yne) (see Figure 1), is based mainly upon the observation of ¹³C scrambling in the biphenylamine product arising from the flash vacuum photolysis of labeled phthalic anhydride and benzocyclobutenedione.¹ Although it is thought that the interconversion is possible, it has



been pointed out recently⁴ that the original experimental evidence¹⁻³ does not offer conclusive proof for the existence of cyclopentadienylidencarbene. Alternative mechanisms were proposed to explain the ¹³C scrambling.

Benzyne has received considerable attention both experimentally and theoretically because of its importance as a reactive intermediate. However, the conflicting characterization of its vibra-

(1) Barry, M.; Brown, R. F. C.; Eastwood, F. W.; Guanawardana, D. A.; Vogel, C. *Aust. J. Chem.* **1984**, *37*, 1643.

(2) Armstrong, R. J.; Brown, R. F. C.; Eastwood, F. W.; Romyn, M. E. *Aust. J. Chem.* **1979**, *32*, 1767.

(3) Hafner, K.; Krimmer, H.-P.; Stowasser, B. *Angew. Chem.* **1983**, *95*, 496; *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 490.

(4) Wentrup, C.; Blanch, R.; Briehl, H.; Gross, G. *J. Am. Chem. Soc.* **1988**, *110*, 1874.

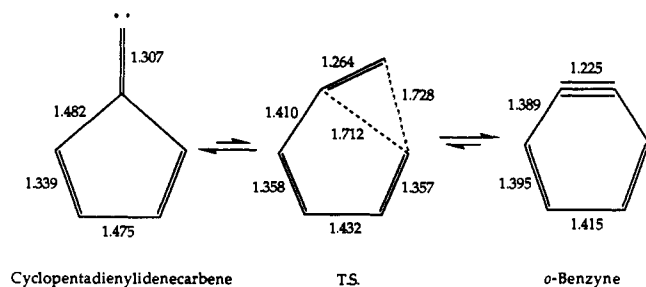


Figure 1. Schematic of the cyclopentadienylidene carbene-*o*-benzyne isomerization with SCF/DZP bond lengths (Å).

tional spectrum, most specifically in the assignment of the $\text{C}\equiv\text{C}$ fundamental stretching frequency, suggests perhaps other contributing fragments. The experimental gas-phase electron photodetachment spectrum of Leopold, Miller, and Lineberger⁵ suggested a very weak $\text{C}\equiv\text{C}$ stretch around 1860 cm^{-1} , an observation in direct conflict with the infrared absorption studies recorded in low-temperature matrices^{4,6} where a band at $2080\text{--}2085\text{ cm}^{-1}$ had previously been assigned to the $\text{C}\equiv\text{C}$ stretching fundamental of *o*-benzyne, with two-configuration SCF (TCSCF)⁹ and MP2⁷ correlated levels giving a value around 1930 cm^{-1} . Its predicted infrared intensity suggests that the mode may be too weak to be detected by conventional infrared techniques.

Further controversy exists in the assignment of the benzyne photoelectron spectrum.¹⁰ High-level *ab initio* studies,¹¹ incorporating both correlation and relaxation effects in the ionization process (with both configuration interaction and Green's function methods), clearly indicate that the band found experimentally at 9.24 eV may possibly arise from another species. The remaining photoelectron spectrum could adequately be assigned to benzyne.

The previous theoretical study¹¹ of cyclopentadienylidene carbene indicated that the reaction from cyclopentadienylidene carbene to benzyne should be exothermic by approximately 14 kcal mol^{-1} as predicted using a 4-31G basis at the STO-3G SCF geometry. No mention was made concerning the transition state or the vibrational spectrum of cyclopentadienylidene carbene.

An extensive theoretical study on singlet cyclopentadienylidene carbene is presented, with the barrier toward rearrangement to benzyne and harmonic vibrational frequencies investigated. Further results are presented for triplet cyclopentadienylidene carbene and the doublet state cyclopentadienylidene carbene anion and cations, allowing the singlet-triplet energy difference, electron affinity, and ionization energies to be investigated.

Theoretical Details

Results are presented for cyclopentadienylidene carbene obtained by using the Huzinaga-Dunning¹³ double- ζ (DZ) basis (with the hydrogen *s* functions scaled by 1.2), also augmented with single sets of polarization functions of exponents $\alpha_d(\text{C}) = 0.75$ and $\alpha_p(\text{H}) = 0.75$, designated the DZP basis. Geometries for cyclopentadienylidene carbene and benzyne were constrained to C_{2v} symmetry and the transition state to C_s sym-

(5) Leopold, D. G.; Miller, A. E. S.; Lineberger, W. C. *J. Am. Chem. Soc.* **1986**, *108*, 1379.

(6) Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J.; Calder, G. V.; Orr, J. G. *J. Am. Chem. Soc.* **1973**, *95*, 6134. Chapman, O. L.; Chang, C.-C.; Kolc, J.; Rosenquist, N. R.; Tomioka, H. *J. Am. Chem. Soc.* **1975**, *97*, 6586.

(7) Scheiner, A. C.; Schaefer, H. F.; Liu, B. *J. Am. Chem. Soc.* **1989**, *111*, 3118.

(8) Radom, L.; Nobes, R. H.; Underwood, D. J.; Li, W.-K. *Pure Appl. Chem.* **1986**, *58*, 75.

(9) Rigby, K.; Hillier, I. H.; Vincent, M. A. *J. Chem. Soc., Perkin Trans. II* **1987**, 117.

(10) Dewar, M. J. S.; Tien, T.-P. *J. Chem. Soc., Chem. Commun.* **1985**, 1243.

(11) Hillier, I. H.; Vincent, M. A.; Guest, M. F.; Niessen, W. von *Chem. Phys. Lett.* **1987**, *134*, 403.

(12) Apeloig, Y.; Schreiber, R.; Stang, P. J. *Tetrahedron Lett.* **1980**, *21*, 411.

(13) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293. Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

Table I. Cyclopentadienylidene carbene Optimized Geometries (Bond Lengths in Å and Angles in deg)^a

	STO-3G SCF	DZ SCF	DZ CISD	DZP SCF
r_1	1.320	1.320	1.336	1.307
r_2	1.489	1.486	1.502	1.482
r_4	1.328	1.350	1.369	1.339
r_6	1.482	1.475	1.489	1.475
t_1	1.080	1.068	1.081	1.073
t_3	1.081	1.069	1.083	1.076
δ_1	127.6	126.9	126.9	126.8
δ_3	109.4	109.5	109.5	109.6
α_1	108.1	107.4	107.4	107.2
β_1	123.7	124.6	124.5	124.8
β_5	126.6	125.8	125.7	125.7

^a See Figure 2 for structural parameter definitions.

Table II. Optimized Geometries for the Transition State from Cyclopentadienylidene carbene to *o*-Benzyne (Bond Lengths in Å and Angles in deg)^a

	STO-3G SCF	DZ SCF	DZ CISD	DZP SCF
r_1	1.279	1.281	1.300	1.264
r_2	1.415	1.406	1.420	1.410
r_3	1.702	1.778	1.803	1.728
r_4	1.349	1.367	1.386	1.358
r_5	1.349	1.363	1.381	1.357
r_6	1.439	1.436	1.451	1.432
r_7	1.763	1.798	1.809	1.712
t_1	1.080	1.067	1.081	1.073
t_2	1.084	1.067	1.081	1.071
t_3	1.082	1.069	1.083	1.076
t_4	1.081	1.071	1.084	1.076
δ_1	171.3	173.4	174.1	175.5
δ_2	70.9	69.9	69.2	67.8
δ_3	111.6	111.9	111.8	111.2
δ_4	116.5	116.5	116.4	115.4
α_1	109.4	109.7	109.6	108.8
α_2	140.4	138.5	139.0	141.3
β_1	122.7	123.1	123.1	122.9
β_3	100.0	97.7	97.0	96.5
β_5	124.7	124.2	124.1	124.4
β_7	121.2	120.6	120.5	120.7

^a See Figure 4 for structural parameter definitions.

Table III. Cyclopentadienylidene carbene DZP/SCF Harmonic Vibrational Frequencies^a (cm^{-1}) and Infrared Intensities (km mol^{-1})

mode	symmetry	freq	IR int	description
1	A_1	3435 (2564)	4	C-H ₁ str (sym)
2	B_2	3431 (2555)	2	C-H ₁ str (asym)
3	A_1	3404 (2516)	4	C-H ₂ str (sym)
4	B_2	3392 (2505)	7	C-H ₂ str (asym)
5	A_1	1864 (1862)	160	C ₁ -C ₂ str
6	B_2	1757 (1691)	1	C ₃ -C ₅ str (asym)
7	A_1	1671 (1631)	30	C ₃ -C ₅ str (sym)
8	A_1	1506 (1335)	14	i.p. H wags
9	B_2	1416 (1245)		i.p. H wags
10	B_2	1220 (1031)		i.p. H wags
11	A_1	1201 (995)	3	i.p. H wags
12	B_2	1172 (904)	14	C ₁ -C ₃ str (asym)
13	A_1	1066 (868)	1	C ₅ -C ₆ str
14	A_2	1041 (865)		ring torsion
15	A_2	1036 (833)		ring torsion
16	A_1	959 (796)	26	C ₁ -C ₃ str (sym)
17	B_2	880 (818)	4	i.p. ring bend
18	A_2	849 (721)	102	ring pucker
19	B_1	796 (622)		ring pucker
20	A_1	711 (685)	1	C ₃ -C ₁ -C ₂ i.p. bend
21	B_1	644 (529)	26	C ₁ o.p.
22	B_1	580 (495)		o.p. ring bend (sym)
23	B_2	219 (213)	12	i.p. ring bend
24	A_2	211 (202)		o.p. ring bend (asym)

^a Deuterated frequencies in parentheses.

metry. Analytic harmonic vibrational frequencies and energies were evaluated by using both the DZ and DZP basis sets at the RHF level.

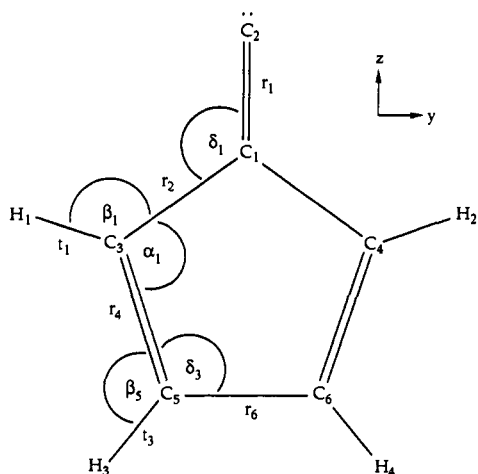


Figure 2. Cyclopentadienylidene carbene coordinate system.

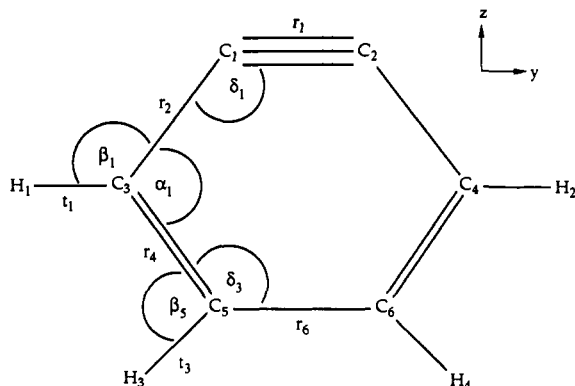


Figure 3. *o*-Benzyne coordinate system.

Geometries were optimized with the CISD (configuration interaction with single and double excitations) method using the DZ basis; however, only CISD single-point energies at the corresponding RHF geometry were possible with the use of the DZP basis. Transition states for the rearrangement of cyclopentadienylidene carbene to benzyne have been located (signified as TS) and characterized at corresponding levels of theory together with isolated benzyne. The CISD expansions consisted of 64 291 (244 041) and 128 089 (423 921) configurations for DZ (DZP) cyclopentadienylidene carbene and TS respectively, freezing the six core orbitals in both cases and deleting the six highest virtuals for the TS. DZP results for benzyne are taken from ref 7. STO-3G¹⁴ energies and geometries have been re-evaluated in this study since insufficient data were presented in ref 12. The triplet states of cyclopentadienylidene carbene, the ²B₂ anion, and cationic states were studied with the larger DZP basis and all computations performed with use of the PSI¹⁵ quantum chemistry codes on the University of Georgia IBM 3090-400E.

Discussion

The bond lengths (Table I) and vibrational frequency analysis (Table III) clearly confirm the simple Lewis structure indicated in Figure 2, with three C=C bonds and three connecting σ bonds. The most interesting feature is the C₁-C₂ carbene double bond which gives an intense infrared band predicted at 1860 cm⁻¹ at the DZP SCF level. (An experimental C₁=C₂ stretching frequency can be estimated by scaling the harmonic frequency by a factor of ~ 0.9 , ref 9 and 16, giving a fundamental experimental frequency probably nearer 1670 cm⁻¹.) Two less intense peaks are noted for the C₃=C₅ bond stretches slightly lower in frequency than the exocyclic C=C, as expected within a ring system. There is also an infrared intense ring pucker mode at 849 cm⁻¹.

The strong infrared double bond stretch is as predicted for a large dipole moment directed along the *z* axis (see Figure 2). The

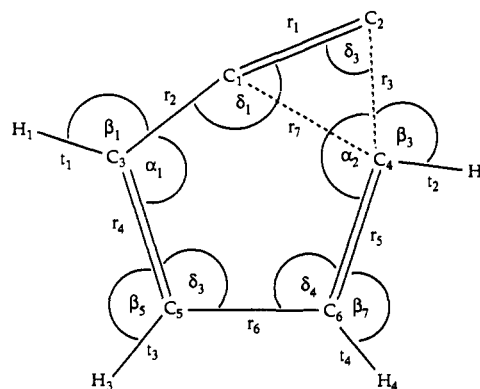
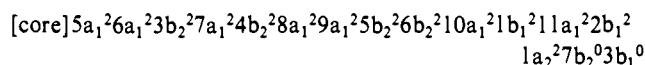


Figure 4. Coordinate system for the transition state for the rearrangement of cyclopentadienylidene carbene to *o*-benzyne.

dipole moment is found to approach 2.3 D, with SCF values predicted to be 1.07, 2.19, 2.30 D with STO-3G, DZ, and DZP basis sets, and a single-reference (SR)CISD value of 2.32 D for the DZ basis.

An important feature in the spectrum is the lack of a fundamental between 1800 and 2200 cm⁻¹, the region predicted for the benzyne C=C stretch. Analytic second derivative analysis with both DZ and DZP basis sets on the \tilde{X}^1A_1 and ³B₂ cyclopentadienylidene carbene, DZP ³B₂ cyclopentadienylidene carbene anion (and DZ X^1A' TS) all indicated that the structures were minima on the potential energy surface (and a true transition state for TS). The optimized geometries are summarized in Table I, and for the transition state in Table II. The electronic structure and bonding for cyclopentadienylidene carbene is essentially straightforward and unlike benzyne can be reasonably described by a single determinant with an electronic configuration:



This is readily shown from the SRCISD calculations where the root CI coefficient is greater than 0.9, second configuration (the 2b₁ → 3b₁ [$\pi \rightarrow \pi^*$] double excitation) and other dominant configurations having coefficients less than 0.05. Limited TCSCF treatments correlating the 7b₂ orbital further confirm this conclusion. The 6b₂ corresponds to an in-plane C₁-C₂ π -type orbital, the 10a₁ a ring π orbital, and the 1b₁ out-of-plane ring π orbital. The outer-valence orbitals are the 11a₁ C₂ lone pair, the 2b₁ (C₁-C₂) + (C₅-C₆) out-of-plane π orbital, and the HOMO, the 1a₂ ring π orbital. The LUMO, 7b₂, is essentially C₂ 2p, and the second LUMO 3b₁ an out-of-plane π^* orbital, as predicted for most alkylidenecarbenes.

The geometrical parameters vary as expected with differing basis set and method: the C-C distances shortening on addition of polarization functions and lengthening when electron correlation is included. The STO-3G and DZ SCF results are expected to reproduce experimental findings quite well due to cancellation of these factors, although no experimental evidence is as yet available. Comparison of geometries for the reaction depicted in Figure 1 shows the rigidity of the C₃-C₅-C₆-C₄ fragment, with nearly all variations accounted for by the movement of the C₁-C₂ fragment. Mulliken charge analyses indicate that the transition state is formed by a simple concerted in-plane ring opening and a neutral 1,2 carbon shift.

Isomerization Barrier

The theoretical barrier heights for the cyclopentadienylidene carbene → benzyne isomerization are presented in Table IV, including both Davidson's correction¹⁷ (CISD+Q) for unlinked quadruple excitations to the CISD energies and SCF zero-point corrections. The energy differences are presented with respect to cyclopentadienylidene carbene, the negative values for benzyne

(14) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

(15) PSI 1.0, 1989, PSITECH Inc., Watkinsville, GA.

(16) Pulay, P.; Fogarasi, G.; Boggs, J. E. *J. Chem. Phys.* **1981**, *74*, 3999.

(17) Davidson, E. R. *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; Reidel: Dordrecht, Holland, 1974; pp 17-30.

Table IV. Relative Energies of Cyclopentadienylidenecarbene (CPI), Benzyne, and the Transition State Connecting Them (kcal mol⁻¹) and Absolute Energies of Cyclopentadienylidenecarbene (hartree)

basis	method ^a	CPI	T.S.	benzyne	total energy
STO-3G	SCF//scf	0.0	20.4	-5.8	-226.538 04
DZ	SCF//scf	0.0	22.2	-8.8	-229.304 83
	CISD//scf	0.0	15.3	-21.8	-229.736 10
	CISD+Q//scf	0.0	14.2	-25.4	-229.804 23
	CISD//cisid	0.0	15.3	-22.1	-229.738 28
	CISD+Q//cisid	0.0	14.2	-25.9	-229.808 26
	zero pt (SCF)//scf	0.0	-0.9	+1.1	
DZP	SCF//scf	0.0	12.7	-8.0	-229.409 49
	CISD//scf	0.0	6.4	-19.3	-230.044 67
	CISD+Q//scf	0.0	5.4	-47.4	-230.151 81
	TC(benzyne)			-34.6	
	CISD//scf				
	TC(benzyne)			-32.4	
	CISD+Q//scf				

^aEnergies at geometries optimized using //method.**Table V.** Vinylidene → Acetylene vs Cyclopentadienylidenecarbene → Benzyne Classical Barrier Comparison (kcal mol⁻¹)

	vinylidene	cyclopentadienylidenecarbene
DZ SCF	26.2	22.2
DZP SCF	14.1	12.7
DZ CISD	17.8	14.2
DZP CISD	7.5	5.4
DZ CISD (+Q)	16.6	13.1
DZP CISD (+Q)	6.6	4.4

indicating benzyne to be the lower energy minimum. At the SCF level, the energy barrier (cyclopentadienylidenecarbene → TS) predicts \tilde{X}^1A_1 cyclopentadienylidenecarbene to be a stable minimum on the PE surface, although the dramatic decrease on inclusion of polarization functions from 22.2 to 12.7 kcal mol⁻¹ is indicative of the inadequacy of the DZ/SCF results. On inclusion of correlation effects at the CISD level, this barrier is also reduced by 6.9 kcal mol⁻¹ with the DZ basis. With the DZ basis set, the three stationary point geometries were reoptimized at the CISD level of theory. It can be seen that using single-point CISD energies at the RHF geometry, as opposed to CISD optimized geometries, has little (0.02 kcal mol⁻¹) effect on the energy difference; hence the single-point DZP/CISD energy differences should be reliable. The 6.3 kcal mol⁻¹ difference between DZP SCF and CISD suggests that the basis set and correlation factors are additive to a first approximation and that the final barrier height may be considerably lower than the DZP/CISD theoretical value. Increased correlation effects, included via the Davidson correction, further lower the barrier at the DZP level by 1.0 kcal mol⁻¹ and the zero-point SCF correction at the DZ level by another 0.9 kcal mol⁻¹. From these values it is possible to predict a final energy difference at nearer 4.5 kcal mol⁻¹, considerably lower than the original DZ SCF difference of 22.2 kcal mol⁻¹.

It is important to consider the extensive theoretical studies on the vinylidene-acetylene isomerization (a 1,2 hydrogen shift), where similar effects have been found and discussed.¹⁸⁻²⁰ A comparison of the energy differences between the unsaturated carbenes cyclopentadienylidenecarbene and vinylidene and the transition states toward isomerization on their respective acetylenes can be found in Table V. The similarity of the TS barrier heights with theoretical method is most striking. A surprising feature is perhaps that the cyclopentadienylidenecarbene barrier, which involves a ring opening and a carbon shift, is lower than the 1,2 hydrogen shift barrier of vinylidene.

As with the vinylidene studies, it is not unreasonable to expect further lowering of this barrier on increasing the basis set size,

(18) Dykstra, C. E.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 1378.(19) Pople, J. A. *Pure Appl. Chem.* **1983**, *55*, 343. Krishnan, R.; Frisch, M.-J.; Pople, J. A.; Schleyer, P. R. *Chem. Phys. Lett.* **1981**, *79*, 408.(20) Gallo, M. M.; Hamilton, T. P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1990**, *112*, 8714.**Table VI.** Cyclopentadienylidenecarbene Anion (²B₂ CPI⁻) and Triplet State (³B₂ CPI) DZP SCF Optimized Geometries (Bond Lengths in Å and Angles in deg)

	² B ₂ CPI ⁻	³ B ₂ CPI		² B ₂ CPI ⁻	³ B ₂ CPI
r ₁	1.318	1.379	δ ₁	127.0	127.6
r ₂	1.483	1.457	δ ₃	109.4	108.3
r ₄	1.338	1.364	α ₁	107.7	109.3
r ₆	1.481	1.454	β ₁	124.4	124.2
r ₁	1.074	1.078	β ₅	126.2	126.5
r ₃	1.076	1.079			

including f-polarization functions or using a more highly correlated wave function. After inclusion of these effects, vinylidene is still predicted to be bound by as little as 3 kcal mol⁻¹,²⁰ probably providing an upper limit for the cyclopentadienylidenecarbene barrier. Extrapolation to an exact barrier with use of this comparison is questionable; however, a classical barrier as low as 1 kcal mol⁻¹ is perhaps not unreasonable.

Evaluation of the relative stabilities of benzyne and cyclopentadienylidenecarbene is more difficult due to the differing levels of theory necessary to describe each entity. Although a final correct analysis of the energy difference between these two molecules necessitates inclusion of the diradical character of benzyne, significant inference can be made from a single-determinant comparison. The results show that there is considerably less emphasis on the choice of basis set; however, correlation effects are more important. The large contribution to the CISD energies from the Davidson correction for benzyne indicates that its CISD wave function constructed with use of a single-root configuration is insufficient. When both configurations of benzyne are included with TC energies taken from ref 7, the energy difference between cyclopentadienylidenecarbene and benzyne is 34.6 kcal mol⁻¹ at the DZP/CISD level. A final difference is predicted at 31.3 kcal mol⁻¹ on inclusion of a Davidson correction of +2.2 kcal mol⁻¹ and a DZ/SCF zero-point correction of +1.1 kcal mol⁻¹. This energy difference is more than double the previous approximate SCF value¹² of 14 kcal mol⁻¹ and the optimized RHF value of 8.0 kcal mol⁻¹ with the DZP basis here. It is apparent that correlation effects are enormously important for this energy difference.

Again, comparison with the vinylidene-acetylene energy difference confirms this value to be more reasonable. At the same level of theory and basis set, ΔE(acetylene-vinylidene) neglecting Davidson and zero-point corrections was found to be 39.5 kcal mol⁻¹. This was raised to a final value of 43 kcal mol⁻¹ at the highest level studied, in agreement with the experimental findings of 44 kcal mol⁻¹.

Triplet States of Cyclopentadienylidenecarbene

The lowest triplet state of cyclopentadienylidenecarbene was found to be the ³B₂ state corresponding to a single excitation from the 11a₁ to the 7b₂ molecular orbital, with a vertical excitation energy at the DZP/SCF level of 29.2 kcal mol⁻¹. Other excited triplets, ³A₂ (2b₁ → 7b₂), ³B₁ (1a₂ → 7b₂), ³B₂ (1a₂ → 3b₁), ³A₁ (2b₁ → 3b₁), and ³B₁ (11a₁ → 3b₁), were found at 41.3, 48.0, 62.3, 73.5, and 100.7 kcal mol⁻¹ respectively above the \tilde{X}^1A_1 state at the \tilde{X}^1A_1 DZP/SCF equilibrium geometry. The DZP/CISD ³B₂ vertical excitation energy is found to be considerably higher than the DZP/SCF value, at 37.8 kcal mol⁻¹ with further increase to 40.2 kcal mol⁻¹ with inclusion of the Davidson correction. The results, of course, reflect that Hartree-Fock theory is better suited for triplets than closed-shell singlet states.

Optimization of the ³B₂ state molecular structure at the RHF level does not significantly affect the excitation energies. The DZP RHF geometry of ³B₂ cyclopentadienylidenecarbene is summarized in Table VI and is largely unchanged compared to \tilde{X}^1A_1 cyclopentadienylidenecarbene. The C₁-C₂ bond length is increased slightly due to occupation of the 7b₂ antibonding orbital, causing a shift in electron density from C₁ to C₂. This bond-length increase is reflected in the lower C₁=C₂ stretch, now at 1786 cm⁻¹ (Table VII) but with a dramatic lowering in infrared intensity to 6 km mol⁻¹ from the \tilde{X}^1A_1 value at 160 km mol⁻¹.

Table VII. Harmonic Vibrational Frequencies^a (cm⁻¹) with Intensities (km mol⁻¹) Predicted for Cyclopentadienylidene-carbene Anion (²B₂ CPI) and Triplet State (³B₂ CPI)

mode	symmetry	² B ₂ CPI		³ B ₂ CPI	
		freq	IR int	freq	IR int
1	A ₁	3369 (2510)	21	3424 (2557)	5
2	B ₂	3361 (2498)	87	3420 (2550)	10
3	A ₁	3337 (2464)	52	3397 (2509)	7
4	B ₂	3319 (2447)	15	3386 (2501)	6
5	A ₁	1624 (1599)	191	1786 (1781)	6
6	B ₂	1670 (1603)	2	1770 (1703)	
7	A ₁	1550 (1496)	160	1682 (1640)	40
8	A ₁	1470 (1349)	165	1499 (996)	14
9	B ₂	1435 (1337)	3	1435 (1058)	
10	B ₂	1259 (903)	15	1271 (1321)	1
11	A ₁	1152 (1041)	52	1192 (871)	1
12	B ₂	1158 (855)	10	1190 (898)	8
13	A ₁	1082 (1022)	10	1058 (1333)	2
14	A ₂	984 (815)		1044 (867)	
15	A ₂	986 (830)	5	1043 (843)	
16	A ₁	983 (791)	66	963 (793)	19
17	B ₂	894 (808)		862 (804)	3
18	A ₂	828 (682)	102	845 (717)	132
19	B ₁	783 (624)		805 (630)	
20	A ₁	728 (691)	1	741 (704)	
21	B ₁	675 (544)	41	650 (533)	18
22	B ₁	626 (527)		570 (485)	
23	B ₂	382 (365)	16	429 (411)	1
24	A ₂	256 (245)	6	237 (225)	2

^a Deuterated frequencies in parentheses.**Table VIII.** Vertical and Adiabatic Singlet-Triplet Energy Separation of Cyclopentadienylidene-carbene (kcal mol⁻¹)

method	cyclopenta-dienylidene-carbene		benzynes
	vertical	adiabatic	
SCF	29.2		
CISD	37.8		
CISD (+Q)	40.2		
SCF	29.1	27.7	
CISD	37.6	32.2	
CISD (+Q)	39.9	33.3	
experiment		37.7	

The singlet-triplet gap predicted for cyclopentadienylidene-carbene is not unexpectedly larger than in benzyne (33.3 kcal mol⁻¹ at the DZP/CISD+Q level, using two-configuration (TC)-CISD+Q energies for ¹A₁ benzyne). The theoretical singlet-triplet ΔE for benzyne agrees well with experiment (37.7 kcal mol⁻¹) and hence we would expect an experimental value for cyclopentadienylidene-carbene only slightly greater than the predicted benzyne energy difference at an analogous level of theory, i.e. 39.9 kcal mol⁻¹.

Electron Affinity of Cyclopentadienylidene-carbene

The ²B₂ state of the cyclopentadienylidene-carbene radical anion has also been studied since the positive electron affinities, generally found in carbenes, can offer more favorable ionic alternatives to their alkyne isomers. The vertical electron affinity of \tilde{X}^1A_1 cyclopentadienylidene-carbene to the ²B₂ cyclopentadienylidene-carbene anion was found at 0.39 eV at the DZP SCF level. At the CISD level this is considerably raised to 0.57 eV (including the Davidson correction). The adiabatic electron affinities are greater by ~0.21 eV (Table VIII), since the DZP SCF geometry of the ²B₂ cyclopentadienylidene-carbene anion is significantly different from that of the neutral species. Both the Mulliken charge analysis and the equilibrium geometry indicate addition of an electron to the 7b₂ unoccupied C₂ 2p_y orbital, causing decreased electron density at the central C₁ atom and the increase in the C₁=C₂ bond. The increase in electron density at C₅ and C₆ is also responsible for the longer C₃=C₅ and C₄=C₆ bonds. These changes are reflected in the vibrational frequency analysis where the C₁-C₂ stretch is lowered to 1624 cm⁻¹ while maintaining its infrared intensity from the neutral species. Increased infrared intensities for the C₃-C₅ symmetric stretch and symmetric i.p.

Table IX. Vertical and Adiabatic Electron Affinity of Cyclopentadienylidene-carbene (eV)

method	vertical	adiabatic
SCF	0.39	0.60
CISD	0.57	0.79
CISD (+Q)	0.57	0.82

Table X. Ionization Energies of \tilde{X}^1A_1 Cyclopentadienylidene-carbene (eV)

	KT	Δ SCF	Δ SCF-CISD	
			cisd	cisd(+q)
1a ₂	9.11	8.07	8.67	8.85
2b ₁	10.04	9.03	9.67	9.83
11a ₁	12.63	9.89	10.43	10.53
1b ₁	14.35			
10a ₁	14.79			
6b ₂	14.87	13.45	13.70	13.70

hydrogen atom wags are noted at 1550 and 1470 cm⁻¹, respectively.

Occupation of the b₂* LUMO is important for both cyclopentadienylidene-carbene and benzyne. In benzyne, where the b₂* corresponds to the in-plane π^* orbital, the singlet-triplet energy difference and electron affinity are both smaller than in cyclopentadienylidene-carbene signifying a lower lying orbital than in cyclopentadienylidene-carbene. This is a large contributing factor for the necessity of a two-configuration wave function for benzyne.

The electron affinity of cyclopentadienylidene-carbene, expected experimentally to exceed the 0.82 eV final adiabatic energy calculated here, compares favorably with the experimental electron affinities of both benzyne⁵ and vinylidene²¹ at 0.56 and 0.47 eV, respectively. As noted by Leopold et al.⁵ in verifying observation of *o*-benzyne and not cyclopentadienylidene-carbene, the electron affinity of this conjugated carbene substantially exceeds that of unsubstituted vinylidene.

Ionization Energies of Cyclopentadienylidene-carbene

The prediction of accurate vertical ionization energies (IE) is notoriously difficult due to the delicate balance between orbital relaxation and electron correlation differences between ion and neutral species.²² The lowest IE for cyclopentadienylidene-carbene was found to correspond to excitation from the 1a₂ orbital at 8.85 eV. A large relaxation energy, from the Δ SCF method, of 1.0 eV is evident which is unlikely to be recovered by the limited correlation recovered by CISD+Q. Koopmans' theorem (KT) energies have often been found to reproduce experimental IEs due to cancellation of the two opposing effects.¹¹ In this case, a large correlation contribution may be expected due to the conjugated nature of cyclopentadienylidene-carbene and an experimental IE exceeding the KT value of 9.11 eV may approach the unassigned 9.24-eV peak in the benzyne spectrum, tentatively proposed to be due to cyclopentadienylidene-carbene by Wentrup et al.⁴ Other theoretical IEs for cyclopentadienylidene-carbene lie above 9.8 eV (Table X).

Conclusions

This study on cyclopentadienylidene-carbene has provided no definite indication for its previous infrared observation or possible existence and finds that cyclopentadienylidene-carbene is a very shallow minimum on the C₆H₄ PE hypersurface. The \tilde{X}^1A_1 ground state of cyclopentadienylidene-carbene is predicted to lie 31 kcal mol⁻¹ above \tilde{X}^1A_1 benzyne, more than double that previously suggested, and is likely to be bound by less than 5 kcal mol⁻¹. The intense exocyclic (C=C) stretch may be observed around 1670 cm⁻¹, a value scaled from the DZP/SCF harmonic frequency at 1860 cm⁻¹. The singlet-triplet energy difference and electron affinity were found to be larger than those observed for benzyne and are predicted for cyclopentadienylidene-carbene at

(21) Burnett, S. M.; Stevens, A. E.; Feigerle, C. S.; Lineberger, W. C. *Chem. Phys. Lett.* **1983**, *100*, 124.(22) Hillier, I. H. *Pure Appl. Chem.* **1979**, *51*, 2183.

40.2 kcal mol⁻¹ and 0.82 eV, respectively, both corresponding to partial occupancy of the 7b₂ LUMO. The lowest IE of cyclopentadienyliidene carbene is predicted to be greater than 8.85 eV, possibly although not conclusively as high as 9.28 eV (corresponding to the unassigned peak in the benzyne photoelectron spectrum).

This study is the highest level study performed on cyclopentadienyliidene carbene so far and clearly provides detail for both

further study and possibly experimental detection.

Acknowledgment. This research was supported by the U.S. National Science Foundation, Grant CHE-8718469. We thank Dr. Yukio Yamaguchi and Dr. Roger S. Grev for their helpful discussions.

Registry No. 2,4-Cyclopentadien-1-ylidene, 4729-01-5; benzyne, 462-80-6.

The Chemical Reaction Molecular Dynamics Method and the Dynamic Transition State: Proton Transfer Reaction in the Formamidine and Water Solvent System

Masataka Nagaoka,* Yoshishige Okuno,^{†,‡} and Tokio Yamabe[†]

Contribution from the Institute for Fundamental Chemistry, 34-4, Takano-Nishihiraki-cho, Sakyo-ku, Kyoto 606, Japan. Received May 31, 1990

Abstract: The chemical reaction mechanism in solution is analyzed by using the chemical reaction molecular dynamics (CRMD) method where a solute molecule and a few solvent molecules are regarded as a supermolecule and the chemical reaction dynamics can be analyzed in a time-dependent way on the intrasupermolecular potential surface. We have examined a proton transfer reaction, the formamidine-water system, and focused on the dynamic effect in the chemical reaction after considering the static "electronic" solvent effect. Two schemes, the constant-temperature scheme (CTS) and the constant-energy scheme (CES), have been employed, and a new type of critical state, named the dynamic transition state (DTS), was found by the appearance of a cusp in the hydrogen-bonding correlation function (HBCF). The cusp is due to the stopping of change in the O-H bond length, which produces a water molecule in the product region. In the CES, alternately modulated oscillation appeared, which is a characteristic in triatomic systems and should play an important role in energy flow in solution. It is emphasized that chemical reaction dynamics should be studied in the phase space by taking the kinetic energy or momentum into consideration.

I. Introduction

The understanding of the molecular dynamics mechanism, i.e., how a chemical reaction in solution takes place, has been one of the most important themes for chemists for a long time. However, because of the complexity of real chemically reacting systems, many analytically unresolved problems still remain.¹⁻³ In recent years, the development of supercomputers has enabled some of those problems to be solved by numerical computation.³⁻¹² Previously, we have focused on the clarification of the static "electronic" solvent effect for chemical reactions by utilizing the supermolecule treatment with the intrinsic reaction coordinate (IRC) analysis,^{4,5} where we have clarified that a special solvent water molecule should participate positively in the whole reaction in order to lower the net potential energy barrier by electron exchange between a solute and a solvent and have suggested that the intrasupermolecular hydrogen-rearrangement mechanism may serve as a fundamental model of double proton transfer mechanism in biochemical systems. Recently, Jorgensen's group regarded a chemical reaction in solution as a dynamical process on a free energy potential surface and developed its treatment for a typical S_N2 reaction in aqueous solution based on the potential of mean force that can be obtained from the radial distribution function by Monte Carlo calculations.^{3,6,7} On the contrary, Benjamin et al. have concentrated on the role of energy fluctuation and transfer (i.e., heat wave) in thermally activated chemical reactions in solution and have examined the path of energy flow through the different modes of the solvent and the reagents for a model atom

exchange reaction in a rare gas solution.^{11,12} However, in the former, the solvent effect was considered only statically by using the potential of mean force for a reactant species by summing up each of the intermolecular potential energies between the reactant and other solvent molecules and by averaging to obtain a radial distribution function.^{1-3,6,7} It is also doubtful whether the intermolecular potential that is prepared between stable molecules is applicable to describe the chemical reaction dynamics in solution, which is, in fact, a common prescription used in most molecular dynamics (MD) studies¹³⁻¹⁵ and might be justified if

(1) Hynes, J. T. In *Theory of Chemical Reaction Dynamics*; Baer, M., Ed.; CRC Press: Boca Raton, FL, 1985; Vol. IV and references therein.

(2) Berne, B. J.; Borkovec, M.; Straub, J. E. *J. Phys. Chem.* **1988**, *92*, 3711.

(3) Jorgensen, W. L. *Adv. Chem. Phys.* **1988**, *70*, 469.

(4) Yamashita, K.; Kaminoyama, M.; Yamabe, T.; Fukui, K. *Theor. Chim. Acta* **1981**, *64*, 303.

(5) Yamabe, T.; Yamashita, K.; Kaminoyama, M.; Koizumi, M.; Tachibana, A.; Fukui, K. *J. Phys. Chem.* **1984**, *88*, 1459.

(6) Madura, J. D.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 2517.

(7) Jorgensen, W. L. *Acc. Chem. Res.* **1989**, *22*, 184.

(8) Ohmine, I. *J. Chem. Phys.* **1986**, *85*, 3342.

(9) Tanaka, H.; Ohmine, I. *J. Chem. Phys.* **1987**, *87*, 6128.

(10) Ohmine, I.; Tanaka, H.; Wolynes, P. G. *J. Chem. Phys.* **1988**, *89*, 5852.

(11) Benjamin, I.; Wilson, K. R. *J. Chem. Phys.* **1989**, *90*, 4176.

(12) Benjamin, I.; Gertner, B. J.; Tang, N. J.; Wilson, K. R. *J. Am. Chem. Soc.* **1990**, *112*, 524.

(13) Giccotti, G.; Hoover, W. G., Eds. *Molecular Dynamics Simulation of Statistical-Mechanical Systems*; North-Holland: Amsterdam, 1986.

(14) Giccotti, G.; Frenkel, D.; McDonald, I. D., Eds. *Simulation of Liquids and Solids. Molecular Dynamics and Monte Carlo Methods in Statistical Mechanics*; North-Holland: Amsterdam, 1987.

(15) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford University Press: New York, 1987.

* To whom correspondence should be addressed.

[†] Also associated with the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Yoshida-moto-machi, Sakyo-ku, Kyoto 606 Japan.

[‡] Permanent address: Daicel Chemical Industries, LTD, 1239, Shinzaike, Aboshi-ku, Himeji, Hyogo 671-12 Japan.