

tangle in Figure 7(a) was shown in Figure 7(b). The distribution of layers with different thickness is analogous with that obtained by the X-ray measurement. The average roughness of LB film, 49.6 Å, calculated using the layer distribution in Figure 4 was well consistent with the mean roughness value (49.8 Å) measured by AFM.

Acknowledgment. This work was supported by the Research Fund on the Optical Technology Project (F-15, 1996) of the Korea Ministry of Science and Technology. The X-ray experiments at PLS, Korea, were supported by MOST and POSCO, Korea.

References

1. Ulman, A. *An Introduction to Ultrathin Films*; Academic Press: San Diego, CA, 1991.
2. Choi, J. W.; Jung, G. Y.; Oh, S. Y.; Lee, W. H.; Shin, D. M. *Thin Solid Films* **1996**, 284/285, 876.
3. Choi, J. W.; Kim, M. J.; Jung, S. W.; Oh, S. Y.; Lee, W. H. *Shin, D. M. Mol. Cryst. Liq. Cryst.* **1996**, 280, 367.
4. Choi, J. W.; Bae, J. Y.; Min, J.; Cho, K. S.; Lee, W. H. *Sensors and Materials* **1996**, 8(8), 493.
5. Choi, J. W.; Kim, M. J.; Jung, S. W.; Oh, S. Y.; Lee, W. H. *Shin, D. M. Mol. Cryst. Liq. Cryst.* **1997**, 294, 217.
6. Choi, J. W.; Min, J.; Jung, J. W.; Rhee, H. W.; Lee, W. H. *Mol. Cryst. Liq. Cryst.* **1997**, 295, 153.
7. Honig, E. P. *J. Colloid Interface Sci.* **1973**, 43, 66.
8. Peng, J. B.; Ketterson, J. B.; Dutta, P. *Langmuir* **1988**, 4, 1198.
9. Momose, A.; Hirai, Y.; Waki, I.; Imazakei, S.; Tomioka, Y.; Hayakawa, K.; Naito, M. *Thin Solid Films* **1989**, 178, 519.
10. Momose, A.; Hirai, Y. *Thin Solid Films* **1991**, 204, 175.
11. Parrat, L. G. *Phys. Rev.* **1954**, 95, 359.
12. Pomerantz, M.; Segmuller, A. *Thin Solid Films* **1980**, 68, 33.
13. Jark, W.; Comelli, G.; Russell, T. P.; Stohr, J. *Thin Solid Films* **1989**, 170, 309.
14. Park, B. J.; Rah, S. Y.; Park, Y. J.; Lee, K. B. *Rev. Sci. Instrum.* **1995**, 66(2), 1722.
15. Segmuller, S. *Thin Solid Films* **1973**, 18, 287.
16. Hwang H. S.; Woo, K. B. *J. of Fuzzy Logic and Intelligent System* **1989**, 2(3), 40.

Structures and Spectroscopic Properties of OC_nO ($n=2-6$): Density Functional Theory Study

Kyung-Hwan Kim, Bosoon Lee, and Sungyul Lee*

Department of Chemistry, Kyunghee University, Kyungki-do 449-701, Korea

Received December 16, 1997

Density functional theory calculations are reported for the carbon clusters bonded with two oxygen atoms OC_nO ($n=2-6$). The structures, vibrational frequencies and dipole moments are computed by BLYP theory with the 6-311G* basis set. Good agreement is obtained between the computed and experimentally observed properties. The ground states of these molecules are shown to be linear. Cyclic structures with higher energy are also predicted.

Introduction

Carbon clusters with polycumululated double bonds of general structure of XC_nY ($X, Y=H_2, O, S$) received considerable attention recently due to the unusual spectroscopic properties and high reactivity. Some of these molecules are known to be very quasilinear.¹ For example, the frequency of the lowest bending mode of the linear molecule OC_3O is only 18 cm^{-1} .² The alternation of the electronic multiplicity (singlet for odd n and triplet for even n) and other properties is also characteristic of these molecules. These molecules are not inherently unstable, and the difficulty of preparing them in laboratory is only due to their unusual reactivity. Quantum chemical treatment of these molecules

were mostly limited to semiempirical or Hartree-Fock level of methods, due to the large size of the molecules. Interstellar detection of carbon clusters also seems to give these molecules astrophysical importance.

Considering the spectroscopic and astrophysical importance of these molecules, we report in the present work the theoretical calculations by employing the density functional theory,^{3,4} which proved⁵⁻⁹ to give surprisingly accurate spectroscopic properties of medium-sized carbon clusters with much less computational efforts than other correlated *ab initio* methods. We report the spectroscopic properties of the carbon suboxides OC_nO ($n=2-6$). We employ the BLYP/6-311G* density functional theory. We find that the ground states of these molecules are linear. The computed spectroscopic properties agree well with experimental observations. Predictions are also made for several cyclic

*Corresponding author

structures.

Computational Methods

In this study all the calculations were carried out using the GAUSSIAN 94 set of programs¹⁰ on DEC 3000/400 work station. The density functional theory with the exchange functional of Becke¹¹ and correlation functional by Lee *et al.*¹² (BLYP), was employed with the 6-311G* basis set. Bond lengths and rotational constants were calculated along with the zero-point vibrational energies and harmonic frequencies.

Results

The energies, rotational constants, and the zero point vibrational energies of the ground states of linear OC_nO (n=2-6) are presented in Table 1. The expected values of the electronic spin $\langle S^2 \rangle$ show that the molecules with odd (even) numbers of carbon atoms are singlets (triplets). This is because OC_nO with odd n has fully filled π orbital (with electronic configuration of ... $\sigma^2\pi^4\pi^4$), while those with even n have π orbitals half filled (... $\pi^4\sigma^2\pi^2$). Calculated bond lengths and harmonic frequencies are reported in Table 2-Table 4. The carbon-carbon bond lengths of these molecules are quite uniform, indicating that they are mostly cumulated double bonds. No scaling factors were employed here to compare with experimental observations. It is very interesting to see that the lowest bending frequencies are very small (less than 100 cm⁻¹ with the exception of OC₂O), verifying the "semirigid" bending nature¹ of these molecules.

The tricarbon suboxide, OC₃O, is a stable molecule, and

Table 1. BLYP/6-311G* energies (a.u.), $\langle S^2 \rangle$, zero-point energies E_0 (kcal/mol) and rotational constants B_e (GHz) of the ground states of OC_nO (n=2-6)

n	Energy	$\langle S^2 \rangle$	E_0	B_e
2	-226.60161	2.0035	8.47	4.2476580
3	-264.72201	0.0000	13.23	2.1763382
4	-302.79631	2.0032	15.09	1.2284357
5	-340.92476	0.0000	19.00	0.7830313
6	-378.96801	2.0033	21.48	0.5222884

Table 2. Bond lengths (Å) and vibrational frequencies (cm⁻¹) of OC₂O

	BLYP/6-311G*	Exp ^b	Exp
r _{O-C}	1.176		
r _{C-C}	1.280		
ν_1 (σ_u)	2352 (2172) ^a		2289.8 ^c
ν_2 (σ_g)	2179 (0)	2196.5	2196.9 ^d
ν_3 (σ_u)	1578 (104)		1587.39 ^e
ν_4 (σ_g)	756 (0)	786.1	787.72 ^f
ν_5 (π_g)	563 (0)	573	580.2 ^g
ν_6 (π_u)	549 (59)		540.24 ^h
ν_7 (π_u)	82 (0)		18.1795 ^h

^a Numbers in parentheses denote intensities, approximated to the nearest integer. ^b Ref. 18. ^c Ref. 19. ^d Ref. 20. ^e Ref. 21. ^f Ref. 22. ^g Ref. 23. ^h Ref. 2.

it is known to be one of the floppiest molecules. The lowest bending frequency is only 18 cm⁻¹, and the barrier from the nonlinear to the linear structure is as small as about 33 cm⁻¹.¹³ The calculated spectroscopic properties are compared in Table 2 with those experimentally measured. It can be seen that the calculated properties in the present work, particularly the harmonic frequencies, are in good agreement with experiments, mostly within 30 cm⁻¹. The lowest harmonic bending frequency (82 cm⁻¹) obtained in our calculations, however, did not reproduce the very low (18 cm⁻¹) experimental bending frequency of the molecule.

For polycarbon oxide sulfides containing more than three

Table 3. Bond lengths (Å) and vibrational frequencies (cm⁻¹) of linear OC₄O and OC₅O

OC ₄ O	BLYP/ 6-311G*	HF/ ^b 3-21 ^d	Exp ^b	OC ₅ O	BLYP/ 6-311G*	Exp matrix	Exp ^c gas- phase
r _{O-C1}	1.188	1.150		r _{O-C1}	1.179		
r _{C1-C2}	1.287	1.268		r _{C1-C2}	1.284		
r _{C2-C3}	1.293	1.268		r _{C2-C3}	1.281		
ν_1 (σ_g)	2283 (0) ^d		2277	ν_1 (σ_g)	2296 (0)	-	-
ν_2 (σ_u)	2135 (1526)		2130	ν_2 (σ_u)	2283 (4677)	2213 ^e	2242
ν_3 (σ_g)	1792 (0)		1816	ν_3 (σ_u)	2049 (437)	2059 ^e	2065
ν_4 (σ_u)	1254 (78)		1276.9	ν_4 (σ_g)	1652 (0)	1665 ^d	-
ν_5 (σ_g)	621 (0)		642	ν_5 (σ_u)	1107 (60)	1144 ^e	1152
ν_6 (π_u)	453 (18)		467.1	ν_6 (σ_g)	544 (0)	573 ^d	-
ν_7 (π_g)	428 (22)			ν_7 (π_g)	526 (0)	530 ^d	-
ν_8 (π_g)	256 (0)			ν_8 (π_u)	523 (20)	539 ^e	542
ν_9 (π_u)	98 (1)			ν_9 (π_u)	429 (22)	470 ^f	474
				ν_{10} (π_u)	153 (0)	145 ^d	-
				ν_{11} (π_u)	48 (0)	-	-

^a Numbers in parentheses denote intensities, approximated to the nearest integer. ^b Ref. 15; Ar matrix. ^c Ref. 14; Ar matrix, infrared. ^d Ref. 24; CCl₄ matrix, Raman. ^e Ref. 24; gas phase.

Table 4. Calculated Bond lengths (Å), and vibrational frequencies (cm⁻¹) of linear OC₂O and OC₆O

OC ₂ O	BLYP/ 6-311G*	CCSD/ DZP ^b	SCF/ DZP ^c	SCF/ DZP ^d	OC ₆ O
r _{O-C}	1.202	1.197	1.168		r _{O-C1} 1.185
r _{C-C}	1.289	1.297	1.281		r _{C1-C2} 1.286
ν_1 (σ_g)	2290 (0) ^d			2653	r _{C2-C3} 1.289
ν_2 (σ_u)	1708 (305)			1954	r _{C3-C4} 1.283
ν_3 (σ_g)	911 (0)			1023	
ν_4 (π_u)	294 (8)			345	ν_1 (σ_g) 2234 (0)
ν_5 (π_g)	216 (0)			277	ν_2 (σ_u) 2214 (3464)
					ν_3 (σ_g) 2056 (0)
					ν_4 (σ_u) 1801 (247)
					ν_5 (σ_g) 1424 (0)
					ν_6 (σ_u) 951 (51)
					ν_7 (π_g) 505 (0)
					ν_8 (σ_g) 474 (0)
					ν_9 (π_u) 470 (23)
					ν_{10} (π_g) 458 (0)
					ν_{11} (π_u) 310 (0)
					ν_{12} (π_g) 133 (0)
					ν_{13} (π_u) 58 (0)

^a Numbers in parentheses denote intensities, approximated to the nearest integer. ^b Ref. 25. ^c Ref. 17. ^d Ref. 26.

Table 5. Relative displacement vectors in the vibrational modes of OC_nO (n=2, 3)

	[-0.16] ^a	[0.16]	[0.16]	[-0.16]	
	O	C	C	O	
(2290) (σ _g)	-.23	.67	-.67	.23	
(1708) (σ _u)	-.42	.57	.57	-.42	
(911) (σ _g)	.64	.29	-.29	-.64	
(294) (π _u)	.42	-.57	-.57	.42	
(216) (π _g)	-.18	.68	-.68	.18	
	[-0.15]	[0.18]	[-0.06]	[0.18]	[-0.15]
	O	C	C	C	O
(2352) (σ _u)	.17	-.53	.61	-.53	.17
(2179) (σ _g)	.32	-.63	.00	.63	-.32
(1578) (σ _u)	-.44	.22	.72	.22	-.44
(756) (σ _g)	.59	.39	.00	-.39	-.59
(563) (π _g)	-.26	.66	.00	-.66	.26
(549) (π _u)	.24	-.57	.49	-.57	.24
(82) (π _u)	.40	-.13	-.81	-.13	.40

^aThe Mulliken charges.**Table 6.** Relative displacement vectors in the vibrational modes of OC₄O

	[-0.14] ^a	[0.11]	[0.03]	[0.03]	[0.11]	[-0.14]
	O	C	C	C	C	O
(2283) (σ _g)	-.17	.47	-.50	.50	-.47	.17
(2135) (σ _u)	-.24	.60	-.28	-.28	.60	-.24
(1792) (σ _g)	-.32	.38	.50	-.50	-.38	.32
(1254) (σ _u)	-.44	.02	.56	.56	.02	-.44
(621) (σ _g)	.55	.42	.16	-.16	-.42	-.55
(453) (π _u)	.24	-.66	.28	.28	-.60	.24
(428) (π _g)	-.26	.63	-.19	.19	-.63	.26
(256) (π _g)	-.16	.12	.68	-.68	-.12	.16
(98) (π _u)	.44	-.03	-.55	-.55	-.03	.44

^aThe Mulliken charges.

carbon atoms, the information is very scarce. OC₄O was the first molecule to be identified¹⁴ of this series containing even number of carbon atoms. OC₅O was first synthesized by Maier and coworkers.¹⁵ These molecules were found to be very reactive but they could be stabilized in organic solvents. The computed structures and the spectroscopic properties of these two molecules are given in Table 3 along with the experimental values. Again, agreement with the experimental results is very good.

Although much efforts have been directed toward synthesizing the simplest of this series of molecules, OC₂O, none was successful. It was only detected¹⁶ as a transient by the neutralization-reionization mass spectrometric technique, and no spectroscopic properties were measured. This molecule was known to have a triplet ground state (³Σ_g⁻).¹⁷ Table 4 compares our computed results for OC₂O with other theoretical results. It can be seen that the harmonic frequencies obtained by HF/DZP method seem to be too large. For example, the highest frequency given in Table 4 (2653 cm⁻¹) is much larger than those experimentally observed for this series of molecules (2200-2300 cm⁻¹). To our best knowledge no report has been made on the spectroscopic properties of OC₆O, which are also presented in Table 4.

Table 7. Relative displacement vectors in the vibrational modes of OC₅O

	[-0.14] ^a	[0.16]	[-0.21]	[0.38]	[-0.21]	[0.16]	[-0.14]
	O	C	C	C	C	C	O
(2296) (σ _g)	.21	-.55	.39	.99	-.39	.55	-.21
(2283) (σ _u)	-.11	.37	-.47	.50	-.47	.37	-.11
(2049) (σ _u)	-.28	.49	.17	-.57	.17	.49	-.28
(1652) (σ _g)	-.34	.23	.58	.00	-.58	-.23	.34
(1107) (σ _u)	-.42	-.11	.37	.59	.37	-.11	-.42
(544) (σ _g)	.52	.43	.23	.00	-.23	-.43	-.52
(526) (π _g)	-.24	.61	-.27	.00	.27	-.61	.24
(523) (π _u)	.25	-.60	.10	.36	.10	-.60	.25
(429) (π _u)	-.07	.13	-.42	.78	-.42	.13	-.07
(153) (π _g)	-.25	.15	.64	.00	-.64	-.15	.25
(48) (π _u)	.45	.05	-.46	-.40	-.46	.05	.45

^aThe Mulliken charges.**Table 8.** Relative displacement vectors in the vibrational modes of OC₆O

	[-0.14] ^a	[0.14]	[-0.22]	[0.22]	[0.22]	[-0.22]	[0.14]	[-0.14]
	O	C	C	C	C	C	C	O
(2234) (σ _g)	.18	-.48	.40	-.27	.27	-.40	.48	-.18
(2214) (σ _u)	-.18	.51	-.43	.16	.16	-.43	.51	-.18
(2056) (σ _g)	.18	-.33	-.11	.59	-.59	.11	.33	-.18
(1801) (σ _u)	-.28	.33	.42	-.37	-.37	.42	.33	-.28
(1424) (σ _g)	.34	-.10	-.53	-.30	.30	.53	.10	-.34
(951) (σ _u)	-.41	-.17	.22	.50	.50	.22	-.17	-.41
(505) (π _g)	.11	-.28	-.09	.64	.64	.09	.28	-.11
(474) (σ _g)	.49	.42	.28	.09	-.09	-.28	-.42	-.49
(470) (π _u)	.24	-.61	.27	.01	.01	.27	-.61	.24
(458) (π _g)	-.22	.54	-.31	.25	-.25	.31	-.54	.22
(310) (π _u)	.11	-.14	-.49	.48	.48	-.49	-.14	.11
(133) (π _g)	-.28	.11	.61	.19	-.19	-.61	-.11	.28
(58) (π _u)	.47	.11	-.30	-.42	-.42	-.30	.11	.47

^aThe Mulliken charges.

Table 5-Table 8 present the Mulliken charges and the vibrational modes of the molecules. It can be seen that the oxygen atoms are of partially negative charge in all of these linear molecules. It is understood that the bending modes (with π symmetry) are doubly degenerate, and that the relative displacements given for these modes represent motions that are along the x axis for one of the doubly degenerate modes, and along the y axis for the other, when the molecular axis is taken to be the z axis.

It was predicted that the polycarbon sulfides C_nS₆ would exhibit alternating properties with the number of carbon atoms in the molecule. The electronic multiplicity (singlet for odd n, triplet for even n) is a typical example. Table 2-Table 4 show an interesting pattern in the bond lengths O-C₁ and C₁-C₂. These bond lengths of OC_nO with odd (even) n are shorter (longer) than those of OC_{n-1}O. Since the molecule with even number of carbon atoms has half-filled π orbitals (triplet states), this indicates that the addition of six electrons and the resulting fully occupied π orbitals (singlet states) strengthen these bonds. This observation also helps understand the alternating pattern in the stretching modes with the highest antisymmetric stretching frequency (σ_u) of OC_nO (1708, 2352, 2135, 2283, 2214 cm⁻¹ for n=2-6).

Table 9. Structures of the cyclic OC₃O and OC₄O (Energy in Hartree, zero-point energy E₀ in kcal/mol, rotational constants B_e in GHz, bond lengths in Å, and angles in degree)

OC ₃ O		OC ₄ O	
Energy	-264.61068	Energy	-302.72028
E ₀	10.35	E ₀	14.67
<S ² >	2.0066	<S ² >	0.0000
r _{O-C1}	1.2015	r _{O-C1}	1.1990
r _{C1-C2}	1.4520	r _{C1-C2}	1.4507
r _{C1-C3}	1.6229	r _{C2-C3}	1.6691
μ	0.0029	μ	0.
B _e	17.5173, 4.4042, 3.2841	B _e	30.2361, 2.3414, 2.1731
∠OC ₁ C ₂	154.4	∠OC ₁ C ₂	144.9
∠C ₂ C ₁ C ₃	56.0	∠C ₂ C ₁ C ₃	70.2

Table 2-Table 4 show that this frequency of OC_nO with odd (even) n is larger (smaller) than that of OC_{n-1}O. Since this stretching mode consists mostly of the motions of the bonds in O-C₁-C₂ moiety (see Table 5-Table 8), this alternating pattern is to be understood in terms of the strengthening of these bonds in the singlet states, which corresponds to the shortening of the O-C₁ and C₁-C₂ bonds (r_{O-C1}=1.2016, 1.1755, 1.1882, 1.1785, 1.1848 Å, and r_{C1-C2}=1.2888, 1.2801, 1.2869, 1.2840, 1.2861 Å for n=2-6). This pattern was also predicted in the ν₁ modes of C_nS (n=2-9).⁹

For carbon clusters with small number of carbon atoms (n ≤ 10), cyclic structures were rarely identified. Observation of cyclic isomers, such as the very recent detection of cyclic C₆ in argon matrix,²⁷ seems to be an important step toward understanding the chemistry of carbon clusters. We searched for cyclic isomers of OC_nO, and found stationary cyclic structures for OC₂O, OC₃O, OC₄O and OC₆O, which are described in Table 9 and Table 10. All of the cyclic structures are planar, and they have different multiplicities (triplet for cyclic OC₃O, and singlet for cyclic OC₄O) than their linear isomers, with the exception of the cyclic OC₂O. This difference in electronic multiplicity for carbon clusters with cyclic carbon skeletons were also observed in OC_nS (n=2-6).⁹

Conclusion

We presented the density functional theory calculations on carbon clusters OC_nO (n=2-6). Good agreement between the computed properties and the experimental observations indicates the efficiency of the BLYP method for medium-sized carbon clusters. We hope that the present calculations would stimulate further investigations on these interesting molecules.

Acknowledgment. This work was supported by the Korea Science and Engineering Foundation (971-0305-032-2 and 95-0501-13-3).

References

- Ross, S. C. *J. Mol. Spectrosc.* **1988**, *132*, 48.
- Burenin, A. V.; Karyakin, E. N.; Krupnov, A. F.; Shapin, S. M. *J. Mol. Spectrosc.* **1979**, *78*, 181.

Table 10. Structures of the cyclic OC₂O and OC₆O (Energy in Hartree, zero-point energy E₀ in kcal/mol, rotational constants B_e in GHz, bond lengths in Å, and angles in degree)

OC ₂ O		OC ₆ O	
Energy	-226.45031	Energy	-378.82652
E ₀	7.35	E ₀	19.92
<S ² >	2.0095	<S ² >	0.0000
B _e	23.5121, 15.2790, 9.2609	B _e	20.7159, 0.8798, 0.8440
r _{O-C}	1.3891	r _{O-C1}	1.1691
r _{O-O}	2.0337	r _{C1-C2}	1.3274
r _{C-C}	1.8927	r _{C2-C3}	1.4740
		r _{C3-C4}	2.0164
μ	0	μ	0
∠COC	85.9	∠C ₁ C ₂ C ₃	136.8
		∠C ₂ C ₃ C ₄	86.3

- Parr, R. G.; Yang, W. *Density Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.
- Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.
- Lee, S. *J. Phys. Chem.* **1996**, *100*, 13959.
- Lee, S. *Chem. Phys. Lett.* **1997**, *268*, 69.
- Lee, B.; So, J.; Lee, S. *Bull. Korean Chem. Soc.* **1996**, *17*, 767.
- Lee, S. *J. Mol. Struct. Theochem* (in press).
- (a) Lee, B.; Lee, S. *Chem. Phys. Lett.* **1998**, *286*, 171.
(b) Kim, K.-H.; Lee, B.; Lee, S. (submitted).
- Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; 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, Inc. Pittsburgh, PA*, 1995.
- Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.
- Lee, C.; Yang, W.; Parr, R. P. *Phys. Rev. B* **1988**, *37*, 785.
- Bunker, P. R. *J. Mol. Spectrosc.* **1980**, *80*, 422.
- Maier, G.; Reisenauer, H. P.; Schäfer, U.; Balli, H. *Angew. Chem.* **1990**, *100*, 590.
- Maier, G.; Reisenauer, H. P.; Balli, H.; Brandt, W.; Janoschek, R. *Angew. Chem. (Int. Eng. Ed.)* **1990**, *29*, 905.
- Süßle, D.; Weiske, T.; Schwarz, H. *Int. J. Mass. Spectro. Ion Processes*, **1993**, *125*, 75.
- Raine, G. P.; Schaefer III, H. F.; Haddon, R. C. *J. Am. Chem. Soc.* **1983**, *105*, 194.
- Carreira, L. A.; Carter, R. O.; Durig, J. R.; Lord, R. C.; Millionis, C. C. *J. Chem. Phys.* **1973**, *59*, 1028.
- Lolck, J. E.; Brodersen, S. *J. Mol. Spectrosc.* **1979**, *75*, 234.
- Lolck, J. E.; Brodersen, S. *J. Mol. Spectrosc.* **1979**, *75*, 445.
- Fusina, L.; Mills, I. M.; Guelachvili, G.; Lolck, J. E.;

- Brodersen, S. *J. Mol. Spectrosc.* **1980**, *79*, 101.
22. Weber, W. H.; Maher, P. D.; Peters, C. W. *J. Chem. Phys.* **1976**, *64*, 2149.
23. Weber, W. H.; Maher, P. D.; Peters, C. W. *J. Mol. Spectrosc.* **1979**, *77*, 139
24. Holland, F.; Winnewisser, M.; Maier, G.; Reisenauer, H. P.; Uhlrich, A. *J. Mol. Spectrosc.* **1988**, *130*, 470.
25. Korkin, A. A.; Balkova, A.; Bartlett, R. J.; Boyd, R. J.; Schleyer, P. V. R. *J. Phys. Chem.* **1996**, *100*, 5702.
26. Sülzle, D.; Schwarz, H. *Angew. Chem.* **1988**, *100*, 1384.
27. Wang, S. L.; Rittby, C. M. L.; Graham, W. R. M. *J. Chem. Phys.* **1997**, *107*, 6032.

Ab initio Studies on Rh(I)- and Ir(I)-Phenylacetylene Complexes

Jeong Hyun Moon, Eun Suk Choi, and Sung Kwon Kang*

Department of Chemistry, Chungnam National University, Taejon 305-764, Korea

Received December 30, 1997

The structures and energies for the intramolecular rearrangement in d^8 - $MCl(PH_3)_2(HC\equiv CPh)$, $M=Rh$ and Ir , complexes were studied by ab initio method at the Hartree-Fock and MP2 levels of theory. Three transition states in two pathways were optimized and characterized by frequency calculations. The activation energies for the process of π -type complex **1** to hydrido-alkynyl **2** have been computed to be relatively low 6.97 and 21.33 kcal/mol at MP2 level for Rh and Ir metals, respectively. However, the activation energies for a 1,2-hydrogen shift via t.s.3 have been computed to be high 50.83 and 60.05 kcal/mol for Rh and Ir metals.

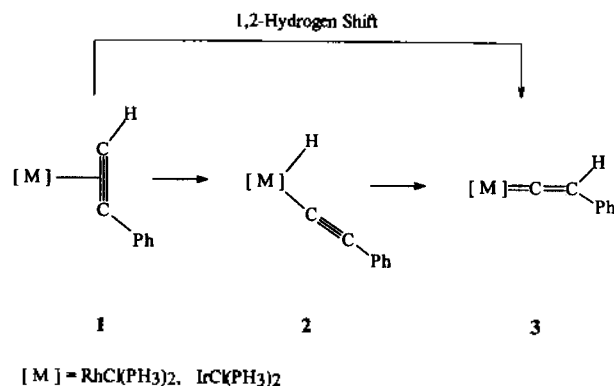
Introduction

The complexation, rearrangement, and liberation of unsaturated hydrocarbons at a transition metals are the most important reaction sequences in both catalytic and stoichiometric organometallic chemistry. There are numerous reports on the transition metal complexes initiating rearrangement of alkyne derivatives to the corresponding alkynyl and vinylidene complexes.¹ As early as 1985, Silverstre and Hoffmann² reported the electronic and geometric features for the process of the rearrangement of transition metal alkynes into vinylidene complexes. The pathway involving hydrido-alkynyl intermediate requires much high activation energy for d^6 - ML_5 fragment at the extended Hückel level. However, they suggested that a direct 1,2-hydrogen shift might be plausible in the metal complex. According to the ab initio calculations by Morokuma and coworkers,³ the 1,2-hydrogen shift mechanism on $RuCl_2(PH_3)_2(C_2H_2)$ system is also supported. Ru metal plays an important role to stabilize the lone pair electrons at the α -carbon atom in the transition state. Another ab initio calculations by Frenking and coworkers⁴ on high oxidation state of Mo and W complexes suggested that the rearrangement of alkyne to vinylidene complexes is thermodynamically unfavorable. Experimentally, there are many evidence for the intermediate alkynyl complexes. It has been reported by Werner and coworkers⁵ that Rh- and Ir-alkynyl complexes, $MCl(PR_3)_2(H)(C\equiv CR')$ where $R'=H, Ph, Me, SiMe_3$, rearrange to the vinylidene complexes and three kinds of isomers have been isolated and characterized. It seems to be interesting to investigate the intramolecular pathways of η^2 -alkyne to vinylidene complex.

We have recently carried out EHT and ab initio molecular orbital calculations on d^8 -acetylene complexes.⁶ We

have focused the electronic and geometric structures of isomers of η^2 - C_2H_2 complex. In this paper we describe the ab initio calculations on the intramolecular pathways (Scheme 1) for $MCl(PH_3)_2(HC\equiv CPh)$, $M=Rh$ and Ir , complexes with potential energy surface.

Computational Methods. All calculations were carried out using the GAUSSIAN 94 packages⁷ on a Cray Y-MP and Indigo 2 workstation. A relativistic effective core potential was used for the core electrons in Rh (up to 4p), Ir⁸ (up to 5p), P and Cl⁹ (up to 2p). The basis sets used were double- ζ for valence region with the contraction scheme (21/21/31) for Rh, (21/21/21) for Ir, and (21/21) for P and Cl. The 3-21G basis¹⁰ was used for the alkyne C and H atoms. And STO-3G¹¹ was used for atoms in phenyl group and the hydrogens in the PH_3 groups. This combination of basis sets is referred to ECP1. A full geometry optimization at the Hartree-Fock (HF) level was carried out and followed single point calculation at 2nd order Moller-



Scheme 1.