

Preferential Site of Attack on Fullerene Cations: Frontier Orbitals and Rate Coefficients

Kee Hag Lee,^{*,†,‡} Changhoon Lee,[†] Jinhee Kang,[†] Sung Soo Park,[#] Jeeyoung Lee,[†] Sang Kuk Lee,[§] and Diethard K. Bohme^{*,||}

Department of Chemistry and Research Institute of Basic Sciences, Wonkwang University, Iksan, Jeonbuk 570-749, S. Korea, CAE Group, Central R & D Institute, Samsung Electro-Mechanics Co. Ltd., Suwon 443-803, Korea, Department of Chemistry, Pusan National University, Pusan 609-735, S. Korea, Department of Chemistry, York University, Toronto, Ontario, Canada M3J 1P3, and Department of Material Science and Engineering, Cornell University, 214 Bard Hall, Ithaca, New York 14853-1501

Received: August 15, 2006

An analysis of reaction efficiency is presented for reactions of carbonaceous ions and molecules. Our results show that the combination of experimental rate-coefficient measurements and computations of the condensed Fukui functions of frontier molecular orbitals and pyramidal angles of π orbitals is very useful for elucidating the reactive sites on fullerene carbon clusters in the gas phase.

1. Introduction

In comparison with normal planar conjugated organic molecules, the fullerenes greatly favor reactions that decrease strain, whereas those reactions that increase strain are inhibited.¹ Fullerene molecules and their ions provide a range of reactive C sites with different degrees of hybridization and strain.^{1,2} Nucleophilic addition^{3–5} and cycloaddition⁶ to C_{70} favor the carbon atoms which have the most pyramidal shape (sites 1 and 2 in Figure 1). Meanwhile, the preferential electrophilic attack⁷ of C_{70} recently observed under Friedel–Crafts conditions ($CHCl_3/AlCl_3$) favors the less pyramidal site of C_{70} (site 4 in Figure 1). Solution studies of the osmylation of C_{70} have identified regioselectivity with different surface strain.⁸ Osmylation occurs mainly at the bond between highly pyramidalized carbons, to a lesser extent at the bond between carbons pyramidalized like those in C_{60} , and little or not at all at the bond between the less pyramidalized carbons.

Investigations with a selected-ion flow tube (SIFT) tandem mass spectrometer⁹ of addition reactions of C_{56}^+ , C_{58}^+ , and C_{60}^+ with NH_3 , C_{56}^{2+} , C_{58}^{2+} , and C_{60}^{2+} with C_2H_2 and CH_3CN , and hydride-transfer reactions¹⁰ of C_{56}^{2+} , C_{58}^{2+} , and C_{60}^{2+} with $n-C_4H_{10}$ revealed an enhanced reactivity for the adjacent-pentagon fullerene ions of C_{56} and C_{58} compared to those of C_{60} . Adjacent pentagons enhance the curvature of the carbon surface of selected C sites.¹⁰ Also, systematic experimental studies of gas-phase addition reactions of C_{56}^+ , C_{58}^+ , C_{60}^+ , C_{70}^+ , corannulene⁺, and coronene⁺ with cyclopentadiene and 1,3-cyclohexadiene¹¹ have shown that the efficiency of bond formation with these two molecules also depends strongly on the curvature of the carbonaceous surface of the reacting cation.^{2,11} For example, the Diels–Alder addition of cyclopentadiene¹¹ is faster with the smaller, more strained fullerene cations, and the efficiencies of addition to the less strained corannulene cation and the flat coronene cation are immeasurably small. Since this

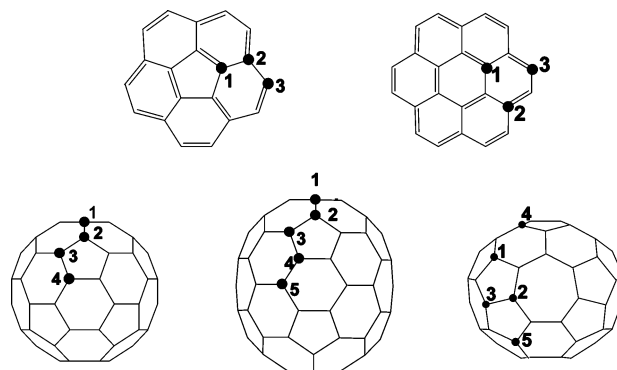


Figure 1. Numbered carbon sites in corannulene, coronene, C_{60} , C_{70} , and C_{58} . See Table 1 for the magnitude of the π -orbital axis vector (POAV) angle at each site for these molecules and their cations.

order of reactivity follows the relative magnitudes of the π -orbital axis vector (POAV) angles, the gas-phase experiments suggest that POAV angles provide a very useful guide for understanding the measured reaction efficiencies.

The π -orbital axis vector (POAV) is defined as that vector which makes equal angles (θ_{OAV}) to the three σ -bonds at a conjugated carbon atom.¹ The POAV angle = $(\theta_{\text{OAV}} - 90^\circ)$ (see Scheme 1) and is 0° and 19.37° for a planar sp^2 and a tetrahedral sp^3 carbon atom, respectively. Table 1 provides a summary of the different POAV angles at the sites of the molecules shown in Figure 1 and their cations. C_{60} has only one such site, while C_{70} has five different types of C sites with different surface strain. The bowl-shaped corannulene molecule has three types of C sites including one without strain, whereas there is no strain in the flat PAH coronene. The corresponding cations have a reduced symmetry except C_{70} . The I_h symmetry of the neutral C_{60} reduces to the D_{5d} symmetry in its cation which has four distinguishable sites.

The POAV analysis of hybridization also has been introduced as a unifying metric for the degree of structural progress in an organic reaction.¹² Here, we extend this concept to find the reaction site (which has a specific POAV angle) from a knowledge of the reaction efficiency. We apply ab initio quantum chemical methods and obtain the frontier function from electronic properties of the highest occupied molecular orbital

* Authors to whom correspondence should be addressed. E-mail: (K.L.) khlee@wonkwang.ac.kr and (D.B.) dkbohme@yorku.ca.

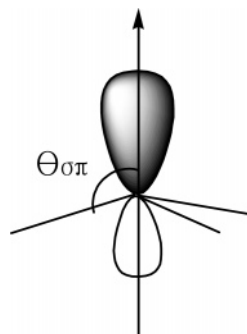
[†] Wonkwang University.

[‡] Cornell University.

[#] Samsung Electro-Mechanics Co. Ltd.

[§] Pusan National University.

^{||} York University.

SCHEME 1: POAV Pyramidalization Angle [$(\theta_{\sigma\pi} - 90^\circ)$, Deg]

TABLE 1: POAV Angles for Various Sites on Selected Carbonaceous Molecules (and Their Cations) and the Indices ($\times 10^3$) of the Condensed Fukui Function of Their Cations in Optimized Structures at the Level of B3LYP/6-31G*^a

sites	C ₆₀	C ₇₀	C ₅₈	corannulene	coronene
1	11.6	11.9	15.2	8.1	0
	(11.7)	(11.7)	(14.6)	(7.5)	(0)
	16	14	33	32	17
2	11.6	11.9	12.7	3.7	0
	(11.8)	(12.0)	(12.2)	(3.3)	(0)
	16	15	25	23	23
3	11.6	11.4	15.5	1.6	0
	(11.7)	(11.5)	(15.7)	(1.8)	(0)
	14	14	23	21	35
4	11.6	10.2	11.3		
	(11.4)	(10.2)	(10.8)		
	20	17	21		
5		8.7	12.0		
		(8.7)	(11.7)		
		9	20		

^a The top number is the POAV angle for the neutral, the number in parentheses is the POAV angle for the cation, and the lowest number is the index of the condensed Fukui function for the cation.

(HOMO) and the lowest unoccupied molecular orbital (LUMO). The POAV should be more useful for predicting the preferred site of attack in these reactions' angle in combination with the frontier function. The frontier function or Fukui function¹³ of chemical reactivity is a local quantity, which has different values at different sites of a molecule. The preferred site of chemical attack is the site with the largest frontier function. The condensed Fukui function is obtained with hybrid density functional theory.

2. Calculations

The structures of the corannulene, coronene, C₆₀, C₇₀, C₅₈, and their cations were optimized with the density functional method (using 6-31G* basis sets) using Becke's three-parameter hybrid method and the Lee–Yang–Parr correlation functional (B3LYP).¹⁴ All geometries at local minima are fully optimized using the Gaussian 03 suite of programs.¹⁵ Our discussion is based mostly on B3LYP/6-31G*//B3LYP/6-31G* (B3LYP/6-31G*) results. The structures that were studied here at the level of B3LYP/6-31G* are those shown in Figure 1. The POAV analysis of the geometrical structures was carried out with the POAV3 program, which is available from QCPE.¹⁶

3. Results and Discussion

The I_h symmetry of the neutral C₆₀ is reduced to D_{5d} symmetry in its cation in our calculations. C₇₀ has the same symmetry, D_{5h} , for both the neutral and its cation. Table 1 gives the POAV angles for various sites on the optimized structures

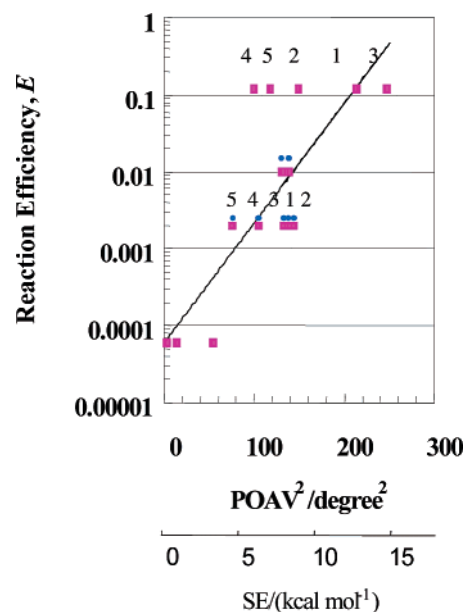


Figure 2. Semilogarithmic plot for the dependence of reaction efficiency (E) on the square of the π -orbital axis vector (POAV) angle for reactions of various carbonaceous cations with cyclopentadiene (squares) and 1,3-cyclohexadiene (circles) in He buffer gas. $E = k_{\text{obs}}/k_c$, where k_{obs} is the measured rate coefficient and k_c is the collision rate coefficient, which is estimated to be $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The numbers of the distinguishable sites are indicated for C_{58}^+ and C_{70}^+ .

of selected carbonaceous molecules and their cations at the level of B3LYP/6-31G*. The POAV angles of coronene and its cation are 0° . Table 1 also includes values for the four and five different carbon sites for C_{60}^+ and C_{70}^+ with structural symmetries of D_{5d} and C_{5h} , respectively. Corannulene has three different carbon sites in its C_{5v} symmetry. However, its cation has C_s symmetry. Table 1 lists the three carbon sites with the largest Fukui functions. For C_{58} which has C_s symmetry, Table 1 provides POAV angles for the five sites (among thirty-one different sites) that have larger coefficients in the HOMO and LUMO than the others.

Figure 2 shows a semilogarithmic plot of the dependence of the previously reported experimental reaction efficiency (E) on the square of the π -orbital axis vector angle for reactions of various carbonaceous cations with cyclopentadiene and 1,3-cyclohexadiene.^{2,11} Here, E is defined as k_{obs}/k_c , where k_{obs} is the measured rate coefficient and k_c is the collision rate coefficient, which is estimated to be $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^{2,11} This plot is drawn on eq 1, which is derived from the experimental data of the reaction efficiency as a function of POAV angles at carbon sites with the largest values of indices of the condensed Fukui function¹³ of selected carbonaceous surfaces at the level of the hybrid density functional (B3LYP/6-31G*) method,

$$k_{\text{obs}} = 6.0 \times 10^{-14} e^{0.60SE} \quad \text{where} \quad SE = 196(\theta - \pi/2)^2 \quad (1)$$

Here, SE is the strain energy¹⁷ at a given carbon atom in kcal mol^{-1} , where θ is the POAV angle in radians. The square of the relation coefficient is 0.999. Equation 1 intercepts the most reactive sites as predicted by the condensed Fukui functions and so should be useful for predicting the reaction sites of other fullerenes.

Figure 2 and eq 1 suggest that the reactions of the C_{58}^+ and the C_{70}^+ cations occur at sites 1 and 4, respectively, of five different carbon sites. These are the sites with the highest indices

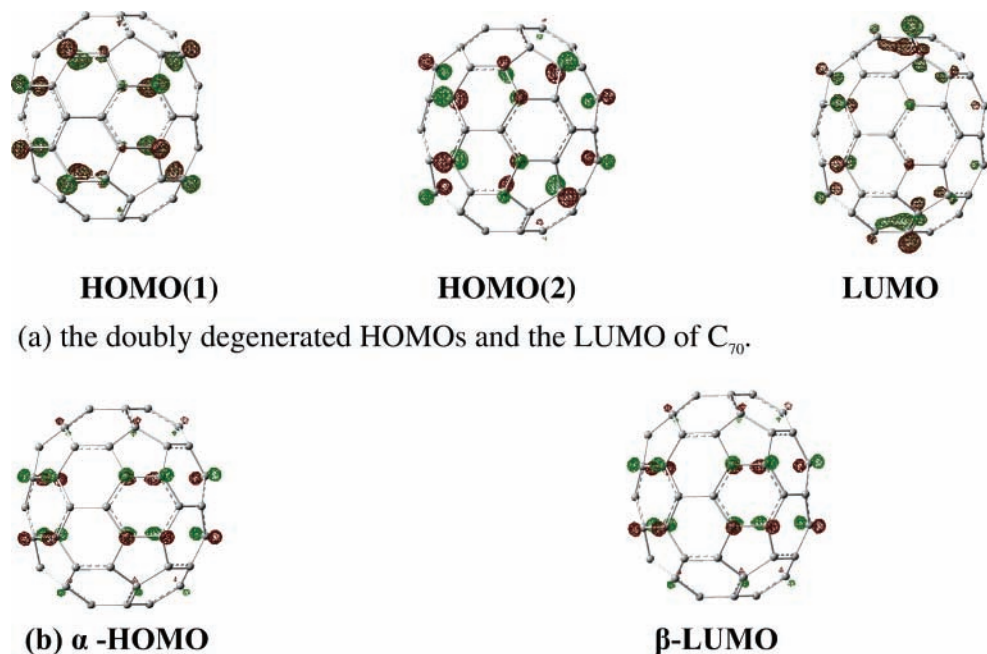
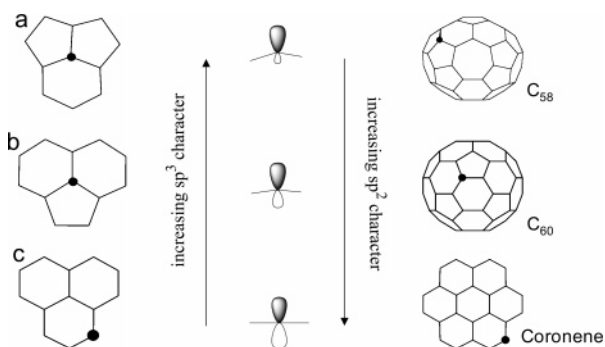


Figure 3. HOMO and LUMO of the C_{70} molecule (a) and its cation (b).

SCHEME 2: Different Orbital Characters at Different Geometrical Environments of Carbon Atoms



of the condensed Fukui functions, and this leads to the important result that the measured rate coefficients (or reaction efficiencies) are useful for confirming the reaction and bonding sites on surfaces of fullerene cations in the gas phase. This preferred reactive site is in line with the lowest energy structure of the alkylated C_{70} cation which was confirmed by NMR measurements and DFT calculations of the relative energies of regioisomers of alkylated C_{70} cation.⁷ Scheme 2 shows the qualitative orbital character at the reaction sites in Table 1. These also suggest that the preference for reaction at a particular C site is not only a function of the highest strain energy (which is the site with the highest local curvature) in those cations by the relief of strain energy but is also a function of the frontier electronic structure of the chemical species.

Scheme 2 is an illustration of different environments for carbon atoms. The formation of a fourth chemical bond to a carbon atom, in a tetrahedral coordination, implies sp^3 hybridization at the carbon concerned in the resulting product. This process is expected to be easiest at sites that already feature a high degree of sp^3 character.

Figure 3 shows the HOMO and LUMO for various sites on C_{70} molecule and its cation at the level of B3LYP/6-31G*. The large LUMO coefficients (Figure 3a) predict that the preferential nucleophilic attack of C_{70} occurs at sites 1 and 2, which have the most pyramidal shape. Meanwhile, the preferential carbon site for electrophilic attack of C_{70} is not clear in the HOMO of

neutral C_{70} , which shows a doubly degenerate state and competition between 6–6 and 5–6 ring junctions. Thus, although the LUMO of the cation could be inferred from the HOMO of C_{70} ,⁷ caution should be exercised if the degenerate HOMO of the neutral is split in the LUMO of its cation.

Figure 3b shows that the HOMO and LUMO for C_{70}^+ have the identical orbital character because the C_{70} molecule and its cation have the same symmetry and the HOMO of the C_{70} molecule is degenerate. The α -HOMO of its cation apparently shows the electrophilic sites of attack of C_{70}^+ that control the addition to the bond common to adjacent five- and six-membered rings. Also, the β -LUMO of its cation clearly shows the nucleophilic sites of attack of C_{70}^+ that control the addition to the bond common to adjacent five- and six-membered rings. Meier and co-workers already reported that addition of benzene to C_{70} produces four adducts, one of which resulted from the addition to such a bond.^{6b} Site 4 and its nearest neighbor sites (see the sites of C_{70} in Figure 1) have bonding character because they have the same lobe direction. These are in line with the predictions made here on the basis of the condensed Fukui function and the POAV angle.

Therefore, our analysis of reaction efficiency shows that the combination of experimental SIFT rate-coefficient measurements and computations of the condensed Fukui functions and POAV angles is very useful for elucidating the reactive sites on fullerene carbon clusters in the gas phase. Also, as far as we know, this is the first demonstration of the combined influence of an electronic effect (the condensed Fukui function) and a geometric effect (the POAV angle) in determining the progress of reactions involving fullerene clusters.

Acknowledgment. This work was supported by the Korea Research Foundation Grant (KRF-2003-015-C00261), in which main calculations were performed by using the supercomputing resources of the Korea Institute of Science and Technology Information (KISTI), and by the BK21 Program of the Ministry of Education and Human Resources Development of Korea. This work (to S.K.L.) was also supported by grant No. (R01-2005-000-10582-0) from the Basic Research Program of the Korea

Science & Engineering Foundation. One of us (K.H.L.) would like to thank Prof. Roald Hoffmann for his warm comment on this paper.

References and Notes

- (1) Haddon, R. C. *Science (Washington, D.C.)* **1993**, *261*, 1545.
- (2) Bohme, D. K. *Can. J. Chem.* **1999**, *77*, 1453.
- (3) Sawamura, M.; Iikura, H.; Hirai, A.; Nakamura, E. *J. Am. Chem. Soc.* **1998**, *120*, 8285.
- (4) Thilgen, C.; Herrmann, A.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2268.
- (5) Wang, Z.; Meier, M. S. *J. Org. Chem.* **2004**, *69*, 2178.
- (6) (a) Bellavia-Lund, C.; Wudl, F. *J. Am. Chem. Soc.* **1997**, *119*, 943.
(b) Meier, M. S.; Wang, G.-W.; Haddon, R. C.; Brock, C. P.; Lloyd, M. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1998**, *120*, 2337.
- (7) Kitagawa, K.; Lee, Y.; Masaoka, N.; Komatsu, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 1398.
- (8) Hawkins, J. M.; Meyer, A.; Solow, M. A. *J. Am. Chem. Soc.* **1993**, *115*, 7499.
- (9) Raksit, A. B.; Bohme, D. K. *Int. J. Mass. Spectrom. Ion Processes* **1983/1984**, *55*, 69. Mackay, G. I.; Vlachos, G. D.; Bohme, D. K.; Schiff, H. I. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *36*, 259.
- (10) Petrie, S.; Bohme, D. K. *Nature (London)* **1993**, *365*, 426.
- (11) Becker, H.; Scott, L. T.; Bohme, D. K. *Int. J. Mass. Spectrom. Ion Processes* **1997**, *167/168*, 519.
- (12) Haddon, R. C.; Chow, S.-Y. *J. Am. Chem. Soc.* **1988**, *110*, 10494. Haddon, R. C.; Chow, S.-Y. *Pure Appl. Chem.* **1999**, *71*, 289.
- (13) Parr, R. G.; Yang, W. *J. Am. Chem. Soc.* **1984**, *106*, 4049. Castellano, E. E.; Piro, O. E.; Caram, J. A.; Mirifico, M. V.; Aimone, S. L.; Vasini, E. J.; Marquez-Lucero, A.; Glossman-Mitnik, D. *J. Mol. Struct. (THEOCHEM)* **2001**, *597*, 163. Tiznado, W.; Chamorro, E.; Contreras, R.; Fuentealba J. *Phys. Chem. A* **2005**, *109*, 3220.
- (14) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
- (15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision B.05; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (16) Haddon, R. C. QCPE 508/QCMP044, POAV3. <http://qcpe.chem.indiana.edu>.
- (17) Haddon, R. C.; Raghavachari, K. *Tetrahedron* **1996**, *52*, 5207.