

중성과 다중 전하를 가진 C₆₀의 상대적 안정도, 이온화 에너지 및 화학 반응성

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Relative Stability, Ionization Potential, and Chemical Reactivity of the Neutral and Multiply Charged C₆₀

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요약. 전편[Bull. Korean Chem. Soc. 1995, 16, 1015]에 기초하여 중성과 다중 전하를 가진 C₆₀ 이온에 대하여 상대적 안정도, 이온화 에너지 및 화학 반응성을 연구하였다. C₆₀¹⁻이 가장 안정하며, 이온화 에너지는 15.31 eV(C₆₀²⁺)로부터 -13.01 eV(C₆₀⁶⁻)까지 값을 갖는다. 또한 전하와 이온화 에너지의 상관 관계에서 직선관계가 나타났으며, 전하당 평균 이온화 에너지는 3.15 eV(계산값)와 3.22 eV(상관관계값)이었다. 양의 전하를 띤 C₆₀ 이온의 전하-이동 및 전자-이동 반응은 게스트 분자의 이온화 에너지가 호스트 C₆₀ⁿ⁺의 전자 친화도보다 더 낮을 때 일어남을 알 수 있었다. 이때, 이온화 에너지와 전자친화도의 에너지 차이(Δ_{IP-EA})가 클 때는 전하-조절 효과에 의하여 전하-이동 반응이 일어나며, 그 에너지 차이가 작을 때는 프론티어-조절 효과에 의하여 전자-이동 반응에 의하여 일어남을 확인하였다.

ABSTRACT. On the basis of our previous paper[Bull. Korean Chem. Soc. 1995, 16, 1015], the relative stability, ionization potential, and chemical reaction of the neutral and multiply charged C₆₀n ions(n=3+ to 6-) have been investigated by the semi-empirical MNDO method. C₆₀¹⁻ has the highest stability. The ionization potential values of the C₆₀ ions range from 15.31 eV of C₆₀²⁺ to -13.01 eV of C₆₀⁶⁻. These values show a linear relationship according to charges. The average IP per charge is 3.15 eV from our calculations and 3.22 eV from the linear function of IP. A charge- or electron-transfer reaction of C₆₀ⁿ⁺ will only occur if the ionization potential of any guest molecule is lower than the electron affinity of the host C₆₀ⁿ⁺. If the energy gap between ionization potential and electron affinity, Δ_{IP-EA} , is high, charge-transfer reactions arise by the charge-controlled effect. However, if Δ_{IP-EA} is low, electron-transfer reactions arise by the frontier-controlled effect.

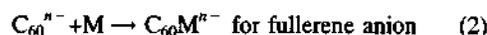
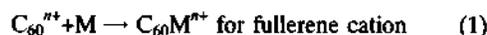
INTRODUCTION

The recent discovery¹ and synthesis² of C₆₀, the fullerene or Buckminsterfullerene, have provoked a widespread investigation into the properties of the molecule. In the circumstances of C₆₀ chemistry, the chemical reactivity of C₆₀ has not been widely studied because it is exceptionally unreactive, unlike ethylene. For the purpose of making C₆₀ de-

rivatives, the reactivity between the charged C₆₀ ion and guest molecules is a very specific area of considerable interest. Also, the unique geometry of C₆₀ and the multiplicity of the multiply charged states of C₆₀ make a fascinating field of fullerene chemistry.

Boheme and co-workers³ have explained that adjacent-pentagon fullerene, C₅₆ and C₅₈, have a high-

er chemical reactivity than the isolated-pentagon fullerene of C_{60} , because adjacent-pentagon fullerenes are substantially lower in thermodynamic stability than isolated-pentagon fullerenes. Smalley and co-workers⁴ have also explained that most smaller fullerenes (C_n with $n < 40$) are found to be more reactive with small molecules such as NO, SO₂, and CO, than the larger fullerenes (C_n with $40 < n < 80$). This inertness of large fullerenes is in accordance with expectations for a closed, edgeless carbon shell with a highly aromatic electronic structure. The chemical reactivities of the neutral and charged C_{60} are reported elsewhere.³⁻⁸ The addition reactions of the charged C_{60} with a guest molecule (M) are as follows;



It has been determined that several factors³ influence the efficiency of reaction (1) for different charged states ($n+$) and for different reactants. The efficiency⁵ of addition reactions shows a dependence upon the ionization potential, the size, and the degree of unsaturation of the molecule. In these addition reactions of the charged C_{60} ion, the chemical reaction of the C_{60} ions provides considerable insight into their structures and physical properties such as ionization potentials and electron affinities.

In our previous paper,⁹ the electronic structures and properties of the neutral and multiply charged C_{60}^n ions ($n=2+$ to $6-$) with spin states were examined by semi-empirical MNDO method. In this work, we have extended the result of the previous work to chemical reactivity including their relative stability and ionization potential for the neutral and multiply charged C_{60}^n ions ($n=3+$ to $6-$).

COMPUTATIONAL METHODS

The same method as in the previous paper⁹ is applied to calculate the properties of the neutral and multiply charged C_{60} ions. The initial geometry of the neutral C_{60} was determined by Santon¹¹ by stereographic projections and a dual graph method.

In this work, the initial structure of C_{60} was generated by using molecular modeling, HyperChem,¹² and the geometry of the neutral C_{60} was completely optimized by using the MNDO method with Polak-Ribiere¹³ optimizer on the symmetry-unrestricted geometry. All the calculations of the multiply charged C_{60} ions have been performed with the semi-empirical RHF MNDO method. The RHF MNDO method can also perform pseudo-RHF calculations for open-shell systems of the multiply charged C_{60} ions. This method is well-known as the RHF half-electron technique.¹⁴ The calculation produces a set of molecular orbitals appropriate for this pseudo-wave function, assigns the unpaired electron with proper spin, and substitutes this electron in the orbital formerly occupied by the half electrons.

Ionization potentials, (SCF), are obtained from total energy differences between the neutral C_{60} and the charged C_{60} ions, calculated at the equilibrium geometry of the neutral C_{60} .

RESULTS AND DISCUSSION

Relative stability. We have calculated the total energy of C_{60}^{3+-6-} at the equilibrium geometry of the neutral C_{60} . These values and the relative energies are listed in Table 1. Relative energies are depicted in Fig. 1. The total energies of the multiply charged C_{60} ions increase in the order $C_{60}^{1-} <$

Table 1. Total energies (E_{tot} /a.u.) and relative energies (E_{rel} /eV) of the neutral and multiply charged C_{60}^n ions ($n=3+$ to $6-$)

n	Energies	
	E_{tot}	E_{rel}
3+	-279.328212	36.49
2+	-279.890873	21.18
1+	-280.340137	8.95
0	-280.669140	0.00
1-	-280.767723	-2.68
2-	-280.749412	-2.18
3-	-280.618383	1.38
4-	-280.370728	8.12
5-	-280.008911	17.97
6-	-279.530762	30.98

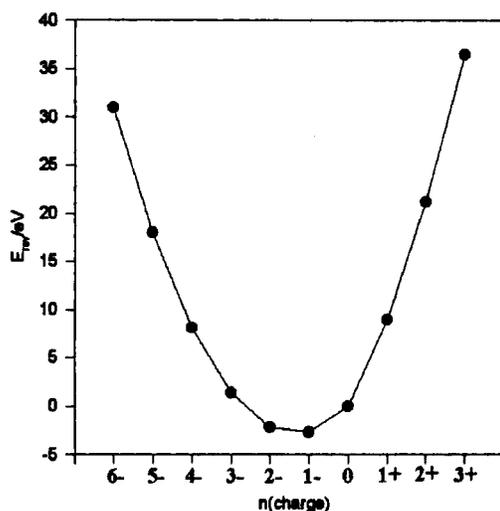


Fig. 1. Relative energies of the neutral and multiply charged C₆₀ⁿ ions (n=3+ to 6-).

$C_{60}^{2-} < C_{60} < C_{60}^{3-} < C_{60}^{4-} < C_{60}^{1+} < C_{60}^{5-} < C_{60}^{2+} < C_{60}^{6-} < C_{60}^{3+}$. It has been estimated that the lowest and highest total energy species among the neutral and multiply charged C₆₀ ions in the ground state are C₆₀¹⁻ and C₆₀³⁺. According to the total energies, C₆₀¹⁻ and C₆₀²⁻ are more stable than the neutral C₆₀. In the view of relative energies, C₆₀³⁺ is less stable than C₆₀ by 36.49 eV and C₆₀⁶⁻ is less stable than C₆₀ by 30.98 eV. However, C₆₀¹⁻ and C₆₀²⁻ are more stable than C₆₀ by -2.68 eV and -2.18 eV.

Our MNDO calculations are the same as *ab initio* calculations^{15,16} and PPP¹⁷ calculations. Clementi and co-workers¹⁵ have suggested that the total energy, E(SCF+B), obtained by adding the correlation energy correction with the Becke algorithms of ground state for C₆₀¹⁺, C₆₀, C₆₀¹⁻ and C₆₀²⁻ are in the order C₆₀¹⁻ < C₆₀²⁻ < C₆₀ < C₆₀¹⁺ on the [(9,5,1)/(4,2,1)] basis set. Chang¹⁶ and co-workers have reported that C₆₀¹⁻ is more stable than C₆₀ and that C₆₀²⁻ is more stable than C₆₀ by 2.5 eV, while C₆₀³⁻ is less stable than C₆₀. Also, Negri and co-workers¹⁷ have published that the relative stability of the neutral and anionic C₆₀ ions increases in the order C₆₀¹⁻ < C₆₀²⁻ < C₆₀ < C₆₀³⁻ < C₆₀⁴⁻ < C₆₀⁵⁻ < C₆₀⁶⁻. C₆₀¹⁻ is the most important among the multiply charged C₆₀ ions, because the

Table 2. Ionization potentials(IP/eV) of the neutral and multiply charged C₆₀ⁿ ions(n=2+ to 6-)

n	IP	
	ΔSCF	Expt.
2+	15.31	.
1+	12.23	12.25 ^a
0	8.95	6.42-7.98 ^b
1-	2.68	2.60-2.80 ^c
2-	-0.50	
3-	-3.57	
4-	-6.74	
5-	-9.85	
6-	-13.01	

^aRef. 27. ^bRef. 26. ^cRef. 24.

most stable C₆₀¹⁻ reacts with NO and O₂.⁷

Ionization potential and electron affinity. Ionization potentials(IPs) are compared with experimental values in Table 2 and presented in Fig. 2. The ionization potential of C₆₀ⁿ⁻ is identical to the electron affinity(EA) of the C₆₀ⁿ⁻¹. The calculated IPs differ from the results of previous studies.¹⁸⁻²² When the IP values of the neutral and multiply charged C₆₀ ions are compared with those of small²³ and organic²⁴ molecules, the IP values of their C₆₀ ions are in the range of positive values(15.31 eV of C₆₀²⁺ to 2.68 eV of C₆₀¹⁻) and negative ones(-0.5 eV of C₆₀²⁻ to -13.01 eV of C₆₀⁶⁻). The small and organic molecules have a narrow range of 9.25 to 15.58 eV²⁵ and 8.01 to 12.98 eV,²⁵ respectively. However the charged C₆₀ ions have a wide range of -13.01 to 15.31 eV. From these results of IPs, it is known that the C₆₀ ions with 2+ to 1- charge are endothermic, but the C₆₀ ions with 2- to 6- charge are exothermic.

For the C₆₀¹⁻ ion, the obtained ionization potential of 2.68 eV is in good agreement with experimental values²⁶ of 2.60 to 2.80 eV and with the predicted values²⁷ of 2.70 to 2.88 eV. The calculated ionization potential of 8.95 eV for the neutral C₆₀ is different from the recent experimental values²⁸ of 6.42 to 7.98 eV. It is known that the neutral C₆₀ has a high IP and high EA. The calculated ionization potential of 12.23 eV for C₆₀¹⁺ is also in good agreement with experimental values²⁹ of 12.25 eV.

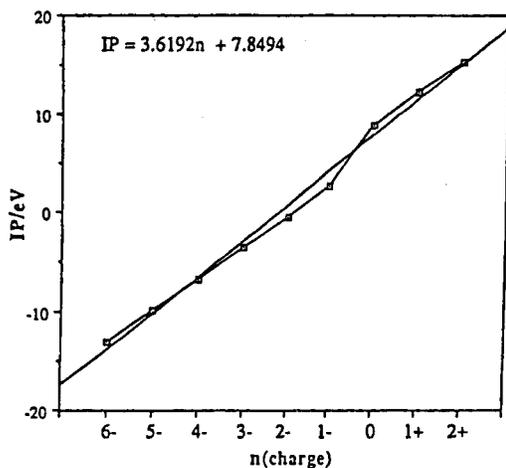


Fig. 2. The relationship of ionization potential with charge of the neutral and multiply charged C_{60}^n ions ($n=2+$ to $-$).

In order to get the relationship between IP and the charge of the neutral and multiply charged C_{60} ions, we plotted the data of IP and n (charge) in Fig. 2 and obtained the fitted linear function of $IP(n)$.

$$IP = 3.6192n + 7.8494 \quad (3)$$

The linear regression value of IP for C_{60} is 7.84 eV, which is in good agreement with 6.42 to 7.98 eV of experimental values. However, that of IPs for C_{60}^{1+} shows a positive error of 0.78 and a negative error of -1.63 and -1.43 compared with experimental values. We have obtained an average IP per charge of 3.15 eV from MNDO method and 3.22 eV from the linear function of IP for the neutral and multiply charged C_{60} .

The relationship between chemical reaction and the HOMO/LUMO energies. Reactivity is determined by a number of factors. Klopman³⁰ and Salem³¹ developed an analysis of reactivity in terms of two factors: an electrostatic interaction approximated by atomic charges and frontier orbital interaction. Fleming³² provided the Klopman-Salem equation that Klopman and Salem derived as an expression for the energy gained and lost when the orbitals of one reactant overlap with those of another using perturbation theory. From Klopman concepts, it has been suggested that a

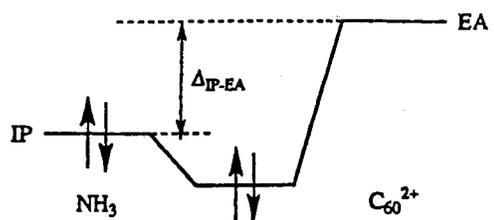
charge-transfer reaction of C_{60}^{n+} will only occur if the IP of any guest molecule is lower than the electron affinity of the host C_{60}^{n+} , known as the charge-controlled effect. Also, electron-transfer reactions will only occur if the IP of any guest molecule is nearly lower than the EA of the host C_{60}^{n+} , known as the frontier-controlled effect.

$$IP(M) < EA(C_{60}^{n+}) \text{ for charge-controlled effect} \quad (4)$$

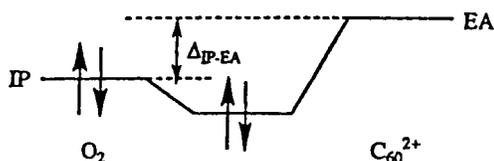
$$IP(M) \leq EA(C_{60}^{n+}) \text{ for frontier-controlled effect} \quad (5)$$

This relation is very similar to frontier orbital,³³ the HOMO and LUMO. From Koopmans' theorem, the IP and EA are related to HOMO and LUMO energy, respectively. That is, $-\epsilon_{\text{HOMO}} = IP$ and $-\epsilon_{\text{LUMO}} = EA$. Hence, the high energy gap between the IP and EA, Δ_{IP-EA} , arises by charge-transfer reactions that govern charge-controlled effect, but the low energy gap inversely arises by electron-transfer that governs frontier-controlled effect. In the chemical reaction of C_{60}^{n+} and a guest molecule having low ionization potential, the role of C_{60}^{2+} is that of an electron acceptor and as a good electrophile by charge- or electron-transfer reaction.

C_{60}^{2+} may undergo charge-transfer reactions with a guest molecule whose IP lies below 12.23 eV. C_{60}^{2+} reacts with NH_3 , having IP of 10.20 eV,²⁵ by charge-controlled effect. The Δ_{IP-EA} between IP of NH_3 and EA of C_{60}^{2+} for the frontier orbitals is 2.03 eV. Also, C_{60}^{2+} reacts with O_2 , having IP of 12.06 eV,²⁵ by frontier-controlled effect. The Δ_{IP-EA} between IP of O_2 and EA of C_{60}^{2+} for the frontier orbitals is 0.17 eV. The Δ_{IP-EA} between C_{60}^{2+} and NH_3 is large but that between C_{60}^{2+} and O_2 is small. Therefore, very little electron transfer occurs in the reaction between C_{60}^{2+} and NH_3 and strong electron transfer occurs in the reaction between C_{60}^{2+} and O_2 . C_{60}^{1+} may similarly undergo charge-transfer reactions with a guest molecule whose IP lies below 8.95 eV. Very recently, Garvey and co-worker⁸ identified that C_{60}^{2+} reacts with guest molecules (NH_3 and O_2). It has been known that C_{60}^{2+} reacts with NH_3 ⁸ but C_{60}^{1+} does not react with NH_3 . The EA of C_{60}^{2+} is larger than the IP of NH_3 but the EA of C_{60}^{1+} is smaller than the IP of NH_3 . These charge- and frontier-controlled ef-



Charge-Controlled Effect



Frontier-Controlled Effect

Fig. 3. Charge- or electron-transfer reaction by governing charge- or frontier controlled effect of C₆₀²⁺ with NH₃ or O₂ molecule having low ionization potential, respectively.

facts between C₆₀²⁺ and guest molecule such as NH₃ and O₂ are presented in Fig. 3.

CONCLUSION

The relative stability, ionization potential, and chemical reaction of the neutral and multiply charged C₆₀ⁿ ions (n=3+ to 6-) have been investigated by the semi-empirical MNDO method. The ionization potential values of the C₆₀ ions range from 15.31 eV of C₆₀²⁺ to -13.01 eV of C₆₀⁶⁻. The average IP per charge is 3.15 eV from our calculations and 3.22 eV from the linear function of IP. A charge- or electron-transfer reaction of C₆₀ⁿ⁺ occurs if the ionization potential of any guest molecule is lower than the electron affinity of the host C₆₀ⁿ⁺. If the energy gap between ionization potential and electron affinity, ΔIP-EA, is high, charge-transfer reactions arise by the charge-controlled effect.

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24. Organic molecules, such as, benzene(9.25), acetylene(11.40), ethylene(10.52), methane(12.98), methanol(10.85), and amine(8.01~8.86). The number of parentheses is ionization potentials in eV adapted from reference 25.
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