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Effect of Addition Groups on the Redox Properties of Fullerenes①

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Abstract Electrochemical properties of fullerene derivatives, including five C_{60} derivatives and four C_{70} derivatives, were studied systematically and comparatively by cyclic voltammetry and differential pulse wave voltammetry. The addition of the electron-donating groups on the fullerenes caused negative shift of the redox potentials of the fullerenes. The extent of the negative shift depends on the number and properties of the addition groups, and on the nature of the fullerenes. 0.08~0.20 V negative shift was observed for C_{60} and C_{70} monoadducts, 0.30~0.32 V for bisadduct and 0.53~0.58 V for triadduct of C_{60}. Meanwhile, the oxidation waves of most of these derivatives appeared on their cyclic voltammograms. Particularly, an irreversible oxidation of the C_{70} bisadduct took place at +0.45 V (vs. SCE), while that of C_{60} bisadduct was at +0.90 V (vs. SCE), indicating that the electronegativity of C_{70} was greatly reduced by the bisaddition of the electron-donating groups.

Key words Fullerenes, Electrochemical properties, Cyclic voltammetry

1 Introduction

Since it was proposed that C_{60} can be derivatized with organic groups while remaining its unique electronic properties[1], the number of synthetic fullerene derivatives increases at a relatively fast pace[1~13]. The work of Wudl et al. is particularly noteworthy, since they have explored rich synthetic chemistry of C_{60} and conducted electrochemical measurement of all of their product[8~13]. These C_{60} derivatives exhibited reversible reduction properties with small negative potential shifts (< 100 mV) relative to C_{60}. For C_{60} and C_{70}, the same redox properties were observed[14]. However, the elctrochemical properties of the C_{70} derivatives have not been studied yet.

The structure of C_{70} is different from that of C_{60}. According to the calculation of Rodunder et al[15], the D_{5h} symmetry of C_{70} is lower than the I_h symmetry of C_{60}, so it would be deduced that the polarity of C_{70} is larger than that of C_{60}, and the effect of the same groups on C_{70} should be of some different from that on C_{60}. In addition, to design new fullerene derivatives for applications to material science and biochemistry, one should know how the additon groups on the fullerene affect its redox properties which can provide a straightforward indication of the electron-acception or electron-donating ability of the fullerence derivatives. It is, therefore, necessary to analyze the electrochemical properties of these

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derivatives systematically and comparatively. Recently, the pyrrolidine mono-, bis- and tri-adducts of C_{60} and those of C_{70} were synthesized in our laboratory[16, 17]. Here we describe the relationship between the structures and redox properties of the derivatives of fullerenes on the basis of the results of cyclic voltammetry and differential pulse voltammetry.

2 Experimental

The preparation and characterization of the derivatives 1～9 of C_{60} and C_{70} (compounds 1～9 in Fig. 1) studied in this paper were reported elsewhere[16, 17]. All their structure and purity have been characterized. Fig. 1 described the structure of the derivatives

Cyclic voltammetry (CV), differential pulse voltammetry (DPV) were carried out with an EG & G Princeton Applied Research (PAR) Model 174A polarographic analyzer and a PAR Model 175 programmer. A three electrode configuration was used throughout. All measurements were performed at ambient temperature under argon atmosphere in a dichloromethane solution containing 0.1 mol·L^{-1} (TEA)BF_4. The concentration of fullerenes and their derivatives is about 10^{-4} mol·L^{-1}. A glass carbon disc with the diameter of 3 mm was used as the working electrode, a platinum plate as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. The electrode potentials on the text are relative to SCE unless otherwise stated.

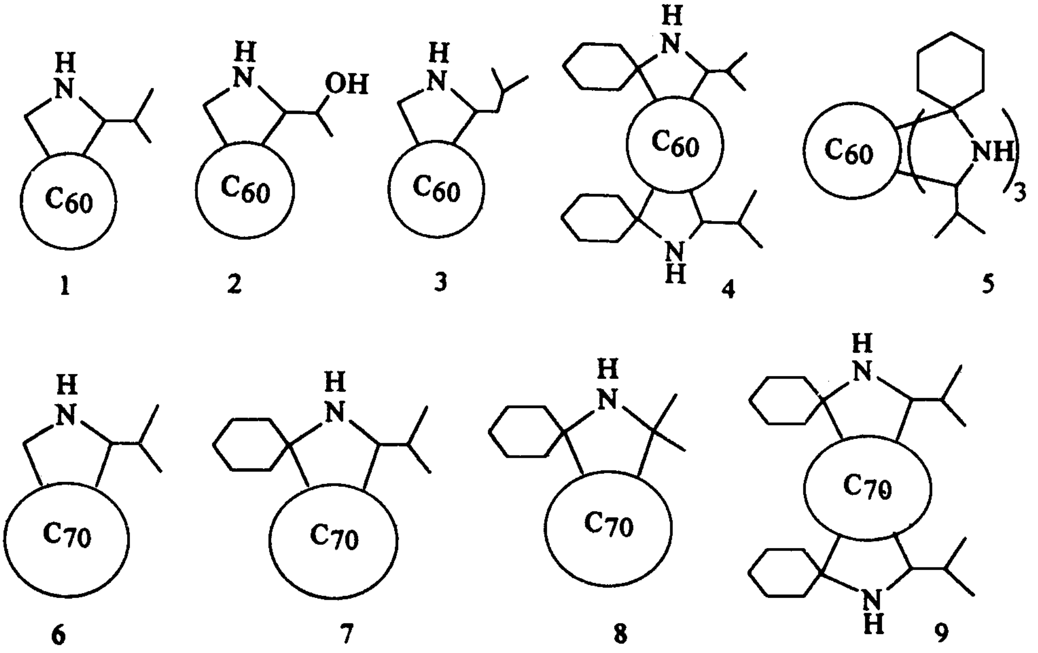

Fig. 1 The structure illustration of compound 1～9 (the derivatives of C_{60} and C_{70})

3 Results and Discussion

The reduction and oxidation potentials of C_{60}, C_{70} and their derivatives, compounds 1～

9 (see Fig. 1), were measured by cyclic voltammetry, which are listed in Tab. 1. All compounds except 9 showd two or three reversible electroreductions in the potential range of 0~ - 1.7 V (Fig. 2) and all except 2 showed one irreversible electrooxidation in the potential range of 0~ + 1.5 V under our condition (Tab. 1).

Tab. 1　Half-wave potentials of C_{60}, C_{70} and their derivatives redox couples in dichloromethane containing 0.1 mol/L (TEA)BF_4 (scan rate: 50 mV/s)

C_{60}, C_{70} and their derivatives (see Fig. 1)	$E_{1/2}$/V (vs SCE) Reduction Steps			Oxidation potential V (vs SCE)
	1st	2nd	3rd	1st
C_{60}	- 0.52	- 0.92	- 1.32	
1	- 0.65	- 1.02	- 1.49	+ 1.30
2	- 0.60	- 1.00	- 1.48	
3	- 0.64	- 1.03	- 1.52	+ 1.35
4	- 0.84	- 1.22		+ 0.90
5	- 1.10	- 1.45		+ 0.87
C_{70}	- 0.50	- 0.90	- 1.27	
6	- 0.64	- 1.03	- 1.44	+ 1.40
7	- 0.70	- 1.07	- 1.44	+ 1.20
8	- 0.70	- 1.08	- 1.43	+ 1.23
9				+ 0.45

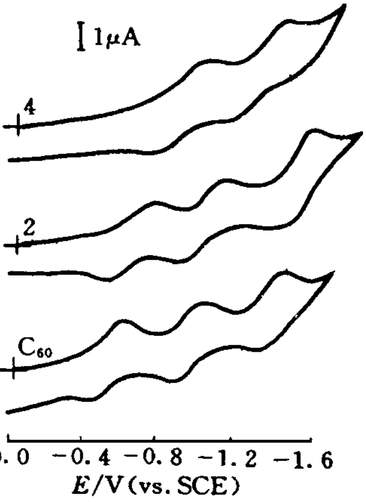

Fig. 2　Cyclic voltammograms of C_{60} and compounds 2, 4 (Fig. 1) at 50 mV/s in dicloromethane containing 0.1 mol·L^{-1} (TEA)BF_4

Monoadducts of C_{60}.　Compounds 1, 2, 3 in Fig. 1 are C_{60} monoadducts. A 0.13 V negative shift of the first reduction wave of compound 1 relative to C_{60} was observed (see Fig. 2 and Tab. 2). The value of the negative shift of the first reduction wave of the C_{60} monoadducts depends on the nature of their addition groups. When a methyl in compound 1 is substituted with a hydroxyl, compound 2 is formed. The negative shift of compound 2 is 0.08 V, indicating that it is more electronegative than compound 1 but still less electronegative than C_{60}. This is reasonable because hydroxyl group is inductively electron withdrawing. If the two methyl's in compound 1 were substituted with one isopropyl, then obtained compound 3 whose negative shift is 0.12 V, a little more electronegative than compound 1. The difference of the negative shift of compounds 1 and 3 is small (≅10 mV), although the electron-donating ability of two methyl groups is greater than one isopropyl group. Probably, the weak effect distinction between two methyl group and one isopropyl group on the negative shift is due to the separation of the alkyl groups from parent C_{60} by a pyrrolidine. In fact, the main effect on C_{60} is determined by the pyrrolidine which attaches C_{60} directly. One can easily recognize that the reduction potentials depend on the electronegativities of the attached atoms[18].

Bis- and triadducts of C_{60}. 0.32 V and 0.58 V negative shifts relative to parent C_{60} were observed for the first reduction of bis- and triadduct of C_{60} (compounds 4 and 5 in Fig. 1) respectively (Tab. 2, and Fig. 2). Owing to the big negative shift, only two reduction peaks in the cyclic voltammograms of compounds 4, 5 were detected in the potential range of 0～ - 1.7 V. We could attribute this significant shift to the following reasons: 1) Cyclichexyl in compounds 4 and 5 is a strong electron-donating group, which shifts the reduction potential to more negative. 2) More than one addition groups can affect the electronegativity of C_{60} remarkably, and this may be the main reason. Comparing the value of the negative shift of the first reduction potential of the mono-, bis- and triadducts of C_{60} mentioned above, it can be suggested that introducing more addition groups is a more effective way to change the electronegativity of C_{60} than prolonging the length of addition groups. In fact, one more addition group in compound 5 shifts the first reduction potential negatively by 0.26 V more than that of compound 4, which is two times of the 0.13 V negative shift of the monoadducts.

Tab. 2 Negative shifts of first reduction potential of compounds 1～8

Compounds 1～8 (see Fig. 1)	The derivatives of C_{60}					The derivatives of C_{70}		
	mono-			bis-	tri-	mono-		
	1	2	3	4	5	6	7	8
ΔE (V)*	0.13	0.08	0.12	0.32	0.58	0.14	0.20	0.20

* For compounds 1～5, ΔE relative to C_{60} and compounds 6～8 relative to C_{70}

Monoadducts of C_{70}. To compare the effect of addition group on C_{70} with that on C_{60}, we obtained the DPV curves of the derivatives of C_{70} (Fig. 3). Compounds 1 and 6 with the same addition group generate almost the same negative shift relative to C_{60} and C_{70} respectively (the shift of the three reduction waves of compound 1 is 0.13, 0.10, and 0.17 V relative to C_{60} and that of compound 6 is 0.14, 0.13, and 0.17 V relative to C_{70}), indicating that the effect of the same group on the monoadducts of C_{60} and C_{70} is identical. For compound 7, adding a cyclichexyl group to the pyrrolidine of compound 6 shifts the reduction potentials more (see Tab. 2) than that of compound 6, which agrees with the result of the C_{60} derivatives (compounds 4 and 5) mentioned previously. It can also be seen from Tab. 2 that the negative shift of the first reduction of compound 8 is 0.20 V, which is the same with that of compound 7. The only difference of compounds 8 and 7 is that the isopropyl in the addition group of compound 7 is substituted by two mathyl groups in compound 8, which is analogous to the C_{60} derivatives of compounds 1 and 3. The results again indicate that the reduction potential shift of the fullerene derivatives is affected mainly by the electronegativity of the attached atoms on the fullerenes[18].

Bisadduct of C_{70}. It is impressive that bisadduct of C_{70} (compound 9 in Fig. 1) is much less electronegative than that of C_{60} (compound 4). For compound 9 no negative waves were observed in its cyclic voltammograms in the potential range of 0～-1.7 V. But for the C_{60} bisadduct (compound 4), the first reduction wave was at -0.84 V and the second was at -1.22 V (see Fig. 2). We may attribute this great difference to the different structure between C_{60} and C_{70}. Although the two fullerenes have the same cyclic voltammetric behavior[14], their structural symmetry is different. If monoaddition group locates in the same electron atmosphere in C_{60} and C_{70}, bis- or trisaddition groups probably show different effect on their distribution. The electron atmosphere in bisadducts of C_{60} which is of perfect symmetry should be more homogeneous than that of C_{70}, then these derivatives of C_{60} are easy to accept the electrons compared with that of C_{70}.

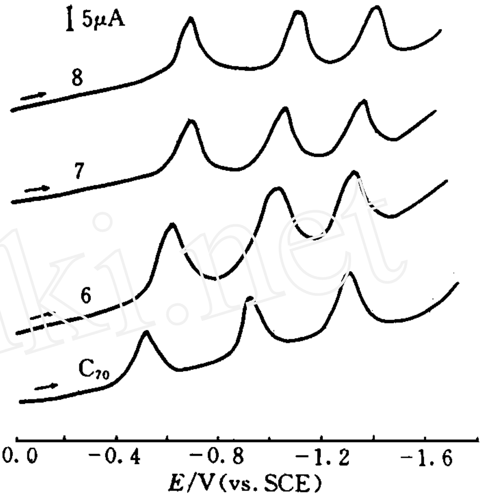

Fig. 3 Differential pulse voltammograms (DPV) of C_{70} and compounds 6, 7 and 8 (see Fig. 1), modulation amplitude: 25 mV, scan rate: 2 mV/s

Oxidation of the adducts of the fullerences As mentioned previously, an irreversible oxidation wave was observed for most of the derivatives in the potential range from 0～+1.5 V vs SCE (see Fig. 4 and Tab. 1). Since no oxidation wave could be obtained below +1.5 V vs SCE for C_{60} and C_{70}, the results indicate that the derivatizating of C_{60} and C_{70} with the addition of electron-donating groups facilitates the electrooxidation process. Electron-donating groups, such as pyrrolidine and alkyl groups significantly lower the oxidation potential of C_{60} and C_{70}. Interestingly, the bisadduct of C_{70}, compound 9, showed a oxidation wave at quite low potential of +0.45 V (vs SCE), while the corresponding derivative of C_{60} (compound 4) was at +0.9 V, and triadduct of C_{60} (compound 5) at +0.87 V in their cyclic voltammograms (Fig. 4). Comparing the oxidation potential of compound 9 with that of compound 7 (see Tab. 1), the addition of one more electron-donation pyrrolidine groups on C_{70} causes its oxidation potential 0.75 V shift negatively.

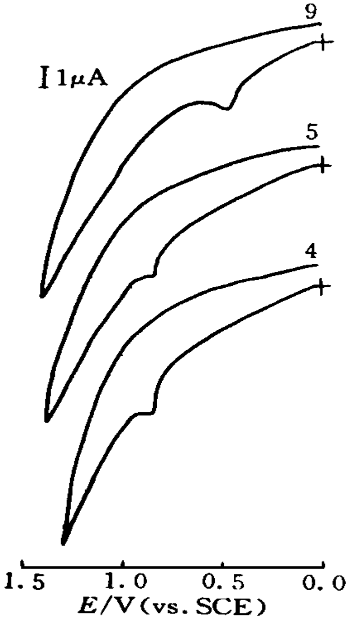

Fig. 4 Cyclic voltammograms of compounds 4, 5 and 9 (see Fig. 1) at 50 mV/s in dichloromethane containing 0.1 mol·L^{-1} (TEA)BF_4

This indicates that the electron-donating ability of C_{70} is greatly increased by the bisaddition.

4 Conclusion

1) The addition of the electron-donating pyrrolidine groups on fullerenes (C_{60} and C_{70}) caused the negative shifts of their redox potentials. For the monoaddition derivatives, the same addition groups have the same effect on the negative shifts of the redox potentials of C_{60} and C_{70}.

2) The more the number of the addition groups on the fullerene, the larger the negative shifts of its redox potentials. The addition of one more pyrrolidine group has stronger effect on the negative shifts than that of previous addition groups.

3) The oxidation of the derivatives took place at a lower potential due to the effect of the addition of the electron-donating groups. A oxidation wave appears at + 0.45 V (vs. SCE) in the cyclic voltammogram of the bisadduct of C_{70}, indicating that compound 9 could be an electron donor.

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加成基团对富勒烯电化学性质的影响

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摘要　采用循环伏安法和微分脉冲伏安法对比地研究了包括五种C_{60}的衍生物及四种C_{70}的衍生物的电化学性质 结果表明, 推电子基团的引入使得富勒烯的氧化还原电位负移, 这种负移的程度与加成基团的性质、个数和富勒烯的性质有关 对于C_{60}和C_{70}的单加成产物, 负移的范围是0.08～0.20 V. 而对于C_{60}的双加成和三加成产物负移的范围分别为0.30～0.32 V 和0.53～0.58 V. 同时由于电位的负移大部分衍生物在低于+1.5 V (vs SCE)观察到了氧化峰, 而C_{60}和C_{70}本身的氧化高达+1.7 V (vs SCE). 特别是对于C_{70}的双加成产物在+0.45 V (vs SCE)出现了一个不可逆氧化峰, 但是, 对于同样加成基团的C_{60}双加成产物的氧化却在+0.90 V (vs SCE), 说明由于推电子基团的双加成引入, 明显改变了C_{70}的电负性

关键词　富勒烯, 电化学性质, 循环伏安