Regioselectively oxygenated $C_{60}O_n$ (n=2,3) isomers

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The oxygenation of fullerene $C_{60}$ with $m$-chloroperoxybenzoic acid ($m$-CPBA) in toluene results in the formation of some regioselective multi-epoxidated $C_{60}$ isomers.[1] Among them, $C_{60}O_2$ is known to have two types of isomers, both with $C_s$ symmetry. Previously, by means of a chromatographic technique using two different columns, we found three types of $C_{60}O_3$ isomers with $C_{3v}$, $C_s$ and $C_2$ symmetry as the predominant products in the reaction solution of $C_{60}$ with $m$-CPBA.[2]

In this study, we isolate those three types of isomers by HPLC separation, and investigated their precise structures by electronic, FT-IR, ^{13}C-NMR and atmospheric pressure photo-ionization (APPI) mass spectra. We also discuss the regioselectivity of epoxidation to $C_{60}$.

The $C_{60}O_3$ isomer with $C_{3v}$ symmetry has three oxygen atoms, which are added onto one benzenoid ring of $C_{60}$ as shown in Figure 1 (**3a**). From our results with ^{13}C-NMR, it was confirmed that other $C_{60}O_3$ isomers with $C_s$ and $C_2$ symmetry have the structure shown in Figure 1 (**3b**) and (**3c**), respectively. The formation ratio of **3a**, **3b** and **3c** was approximately 1:1:1.

On the other hand, the structure of the major isomer in $C_{60}O_2$ is known to be symmetrical with $C_s$, where two oxygen atoms are attached to one benzenoid ring of $C_{60}$ as shown in Figure 1 (**2a**).[3] The structure of the minor isomer has not been clarified yet. Our ^{13}C-NMR spectrum for the isolated minor isomer had three peaks, at 67.6, 78.7, and 82.3 ppm in the $sp^3$ region. This result suggested that the minor $C_{60}O_2$ isomer has the structure shown in Figure 1 (**2b**), because any diepoxidated $C_{60}$ isomer, except for that shown in **2b**, is expected to show two peaks in the $sp^3$ region. The formation ratio of **2a** to **2b** was $ca$. 8:2.
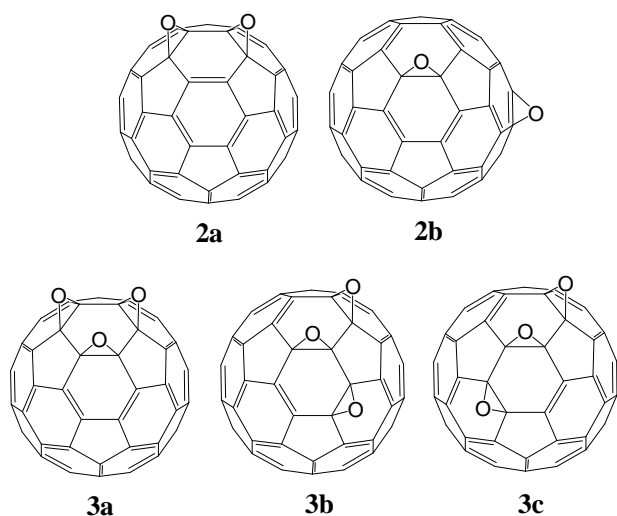


**2a**          **2b**

**3a**          **3b**          **3c**

**Figure 1.** The structures of the two types of $C_{60}O_2$ isomers and three types of $C_{60}O_3$ isomers formed by $m$-CPBA oxidation of $C_{60}$.

The structures of $C_{60}O_n$ (n=2,3) isomers (**2a**, **2b**, **3a**, **3b**, **3c**) are in agreement with our prediction from the static reaction index calculation for the addition sites of the epoxy groups to $C_{60}$. The electrophilicity of $m$-CPBA is attributed to its relatively weak O-O bond, which can provide an empty $\sigma^*$ orbital with the nucleophilic $\pi$-bond of $C_{60}$. Usually, conjugated alkenes undergo epoxidation less easily than non-conjugated alkenes. In the case of

fullerene, electrophilic oxygen can be easily added to double bonds due to its distorted structure. The electrophilic oxygen tends to attack the bond with a high electron density. In the same way, the epoxidation of fullerene by the electrophilic oxygen of $m$-CPBA occurs on the electron-rich double bonds. Consequently, the electron density of a bond is expected to give a good index of a probable reaction site. Therefore, a calculated relative yield of the $j$-th isomer of $C_{60}O_n$, $Y_{(n,j)}$, can be calculated as follows:

$$Y_{(n,j)} = \sum_{i=1}^{m} Y_{(n-1,i)} P_{(i,j)} \qquad (1)$$

The branching probability $P_{(i,j)}$ is defined by utilizing the difference between the electron density of the bond of addition site $j$ and the constant. We assumed that the branching probability increases linearly with the difference in electron density ($b_j$-$c$) as shown in the following.

$$P_{(i,j)} = \frac{d_j(b_j - c)}{\sum_{k=1}^{i} d_k(b_k - c)} \qquad (2)$$

The results of our calculation for $C_{60}O_2$ and $C_{60}O_3$ are shown in Table 1 and Table 2, respectively. According to our calculation, the possible $C_{60}O_2$ isomers are only **2a** and **2b**. This agrees with our experimental results. Our calculation predicted the relative yields of **2a** and **2b** to be 88% and 12%, respectively, which agree with our experimental yields of $ca$. 8:2. The predominant $C_{60}O_3$ isomers in our calculation were the same as the three types of isomers, **3a**, **3b** and **3c**, found in our experiment. It is believed that most $C_{60}O_3$ isomers produced by $m$-CPBA epoxidation were formed from **2a**.

**Table 1.** The calculated percentage yields and point group of the possible isomers of $C_{60}O_2$.

| Isomer | Relative Yield (%) | Symmetry |
|--------|--------------------|----------|
| **2a** | 88 | $C_s$ |
| **2b** | 12 | $C_s$ |

**Table 2.** The calculated percentage yields and point group of the possible isomers of $C_{60}O_3$.

| Isomer | Relative Yield (%) | Symmetry |
|--------|--------------------|----------|
| **3a** | 18 | $C_{3v}$ |
| **3b** | 27 | $C_2$ |
| **3c** | 37 | $C_s$ |

We also studied the formation of $C_{60}O_n$ by oxygenation using ozone. Although ozone formed two types of $C_{60}O_2$ isomers in the same manner as $m$-CPBA, the formation yields of **2a** and **2b** were different. The major $C_{60}O_2$ isomer by ozone epoxidation was evidently **2b**. The formation mechanism of $C_{60}O_x$ (x>2) in ozone epoxidation is likely to be different from that of $m$-CPBA epoxidation. It is possible that the ozonide of $C_{60}$,[4] the reaction intermediate, obstructs the next oxygenation of adjoining double bonds due to the steric hindrance.

**References**
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