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Reactions of Anionic Oxygen Nucleophiles with C_{60} Revisited

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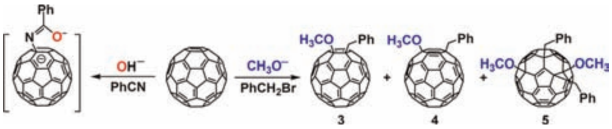
ABSTRACT



Reactions of C_{60} with oxygen nucleophiles of HO^- and CH_3O^- are revisited in PhCN in the presence of $PhCH_2Br$. Different from previous results that such reactions lead to the formation of complex mixtures, well-structured C_{60} oxazolines are obtained when HO^- is involved, while di- and tetraadducts with methoxy and benzyl addends are obtained when CH_3O^- is engaged. The reactions are followed by in situ vis–near-IR spectroscopy, which reveals further information for the reactions.

Fullerenes, represented by C_{60}, are electron-deficient molecules and are favorable for reactions with nucleophiles.[1] However, the so far well-established nucleophilic reactions for fullerenes are mostly based on carbon nucleophiles, including organometallic reagents,[1–11] a cyanide anion,[12] depronated α-halo esters or ketones for Bingel reactions,[13,14] and transition metal catalyzed arylation and allylation reactions,[15,16] while reactions with oxygen nucleophiles such as hydroxide and alkoxide anions are often overlooked, since such reactions usually result in complex mixtures rather than well-structured organofullerenes.[1,17–20]

Even though methoxylated C_{60} adducts can be detected in ESI MS, no products have been actually isolated and characterized from the reaction mixtures.[20,21] Consequently, the preparations of alkoxylated fullerene derivatives are usually achieved via either substitution reactions of halogenated fullerenes[22–24] and fullerenol,[25] or via photoinduced radical reactions,[26] rather than direct

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nucleophilic additions to fullerenes. Wang and co-workers have shown that the presence of O_2 is crucial for the production of well-defined compounds from the reactions of C_{60} with alkoxide anions, where C_{60}-fused 1,3-dioxolane and tetrahydrofuran derivatives can be obtained.[27–29] Meanwhile, Gan et al. have shown that monomethoxylated and multiple methoxylated C_{60} derivatives can be produced via nucleophilic additions of methoxide to C_{60} derivatives with peroxide adducts.[30] However, to the best of our knowledge, no work has appeared on the preparation of alkoxylated fullerene derivatives via direct addition of alkoxide anions to pristine fullerenes to date. Apparently, the reactions of C_{60} with anionic oxygen nucleophiles are still not well understood and are very much neglected as a synthetic approach for fullerene functionalizations.

Herein, we report the reactions of C_{60} with hydroxide and methoxide anions. Unexpectedly, C_{60} oxazolines (compounds **1** and **2**) are formed from the reactions of HO^- with C_{60} and PhCN via an anion relay mechanism; while methoxylated fullerenes (compounds **3**, **4**, and **5**) are formed via the direct nucleophilic additions of a methoxide anion to C_{60} followed by subsequent electrophilic addition of $PhCH_2Br$.

The nucleophilic addition of OH^- to C_{60} was examined in PhCN with the use of 1.0 M TBAOH (tetra-*n*-butylammonium hydroxide)/CH_3OH solution as the OH^- source. The color of the solution changed gradually from purple to completely green after addition of TBAOH/CH_3OH, and the reaction was finished by quenching with either I_2 or $PhCH_2Br$, leading to compound **1** (43%) or **2** (30%) respectively (see Supporting Information for details).

The identities of compounds **1** and **2** are established on the basis of NMR, MS, HPLC, and UV–vis characterizations in light of reported data.[31–34] The formation of C_{60} oxazolines from OH^- addition to C_{60} in PhCN is quite unexpected, since no such compounds have been reported from reactions carried out under similar conditions,[21] and the addition of OH^- to C_{60} has been intended mainly as an approach to prepare fullerenols.[17–19] The in situ vis–near-IR was therefore carried out to obtain a better understanding of the reaction.

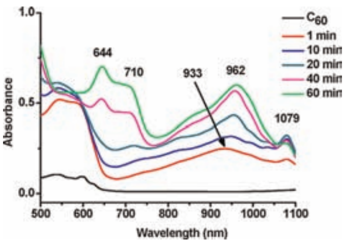

Figure 1. In situ vis–near-IR spectra for the reaction of C_{60} (1.3×10^{-4} M) with 3 equiv of TBAOH in PhCN at different reaction times under deoxygenated conditions at rt.

Figure 1 shows the in situ vis–near-IR spectra for the reaction of C_{60} with TBAOH and PhCN at different reaction times under deoxygenated conditions at rt. A broad absorption band at 933 nm appears immediately following the addition of 1.0 M TBAOH/CH_3OH into C_{60} PhCN solution. As the reaction proceeds, the intensity for the broad absorption band keeps increasing but is red-shifted to 962 nm, along with the appearance of new strong absorption bands at 644 and 710 nm. Komatsu and co-workers have shown that a dianionic singly bonded C_{60} intermediate of $C_{60}^{-}{-}C{\equiv}C{-}C_{60}^{-}$ exhibits a strong absorption at 965 nm,[35] which matches well with the 962 nm absorption band in Figure 1, indicating that a dianionic singly bonded intermediate is probably present. Previous work has suggested that $\mathbf{1}^{2-}$ is a singly bonded dianion;[33] it is therefore reasonable to assign the absorption band at 962 nm to $\mathbf{1}^{2-}$. The assignment is confirmed by the near-IR spectrum of $\mathbf{1}^{2-}$ (Figure S3), which shows absorption bands at 963, 710, and 645 nm, in excellent agreement with the spectrum of the reaction mixture at 60 min as shown in Figure 1, indicating that the nucleophilic addition of OH^- to C_{60} in PhCN almost exclusively leads to the formation of a C_{60} oxazoline dianion. In fact, the yield of C_{60} oxazolines obtained from this method is much higher compared to that obtained via aerobic oxidations of anionic C_{60},[31,34] even though there are still toluene insoluble materials formed from the reaction, which are likely produced via polymerization of anionic oxygenated C_{60} species.[36,37]

An absorption band corresponding to $C_{60}^{\bullet -}$ is also shown at 1079 nm,[38] which is probably produced via electron transfer from ROC_{60}^{-} ($R = H$ or CH_3) to C_{60} as proposed previously.[11,21] However, the intensity of the peak is rather weak, indicating that the amount of ROC_{60}^{-} is very slight, implying that the reaction mixture of C_{60}, OH^-, and PhCN is an overall dianionic system rather than a monoanionic one.

We have recently shown that C_{60} oxazolines can be produced via aerobic oxidation of C_{60}^{2-}, where $\mathbf{1}^{2-}$ is

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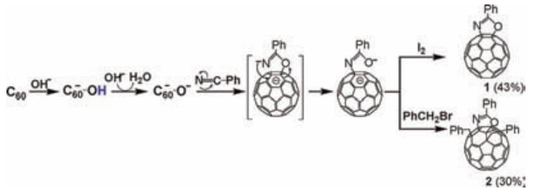
Scheme 1. Proposed Mechanism for the Formation of C_{60} Oxazolines via the Reaction of C_{60} with TBAOH and PhCN



formed via the key intermediate of $C_{60}{}^{-}{-}O^{-}$.[34] Since $\mathbf{1}^{2-}$ is also shown to form during the reaction of C_{60} with OH^{-} and PhCN, it is likely that the reaction proceeds via a similar mechanism with the formation of the key intermediate of $C_{60}{}^{-}{-}O^{-}$. A reaction mechanism for the nucleophilic addition of OH^{-} to C_{60} in PhCN is therefore proposed as shown in Scheme 1, where the C_{60} oxazolines are formed via an anion relay mechanism initiated by the nucleophilic addition of OH^{-} to C_{60}.

In addition to the nucleophilic nature, the hydroxide anion is also a strong base and has been extensively used to abstract the fullerenyl proton from HRC_{60} (R = alkyl or H).[39,40] It is therefore likely that $C_{60}{}^{-}{-}OH$ is formed first via the nucleophilic addition of OH^{-} to C_{60}, then $C_{60}{}^{-}{-}O^{-}$ would be formed via subsequent deprotonation of $C_{60}{}^{-}{-}OH$ by OH^{-} owing to its strong basic nature. The resulting $C_{60}{}^{-}{-}O^{-}$ would then attack PhCN to form an anionic imine species, which would then attack back at the C_{60} sphere accompanied by a heterolytic cleavage of the $C_{60}{-}O$ bond to form $\mathbf{1}^{2-}$, leading to the formation of **1** or **2** upon quenching with I_2 or $PhCH_2Br$. The results indicate that, for the nucleophilic additions of OH^{-} to fullerenes, the OH^{-} functions as not only a nucleophile but also a strong base.

Interestingly, when $PhCH_2Br$ was first added into C_{60} PhCN solution before adding 1.0 M $TBAOH/CH_3OH$ solution, C_{60} reacted with CH_3O^{-} and $PhCH_2Br$, leading to methoxylated products **3**, **4**, and **5**, rather than the reaction involving OH^{-}, with no compound **2** formed. The reaction was affected by the temperature, and a yield of 29%, 10%, and 27% was obtained for **3**, **4**, and **5** when the reaction was performed at 50 °C, which was better than the case when the reaction was carried out at rt. It is noteworthy that under such conditions, $PhCH_2Br$ could also react with OH^{-} or MeO^{-}, competing with C_{60}.

The HRMS of **3** and **4** indicate that both compounds have the formula $(CH_3O)(PhCH_2)C_{60}$. The configurations of two compounds are further established with UV/vis and NMR characterizations. The UV/vis spectra of **3** (Figure S6) and **4** (Figure S12) exhibit absorptions at 431 and 443 nm respectively, which are characteristic for the 1,2-[41,42] and 1,4-adduct of C_{60}.[26,42,43] The ^{13}C NMR spectra of **3** and **4** display 28 and 45 resonances respectively for the sp^2 carbons of C_{60}, indicating that they have C_s and C_1 symmetry respectively. The HMBC NMR of **3** (Figure S10) shows that the methylene protons have cross peaks not only with the C_{60} sp^3 C-atom (67.2 ppm) bonded to the benzyl but also with the C_{60} sp^3 C-atom (93.3 ppm) bonded to the methoxy, confirming that the molecule is a 1,2-adduct for **4**, the resonances for the sp^3 C_{60} carbons bonded to the benzyl and methoxy groups appear at 59.27 and 80.47 ppm, which are in good agreement with the reported values for $1,4\text{-}(PhCH_2)_2C_{60}$ (60.2 ppm)[42,43] and $1,4\text{-}(CH_3O)RC_{60}$ (around 80 ppm),[22,25,26] indicating that **4** is a 1,4-adduct.

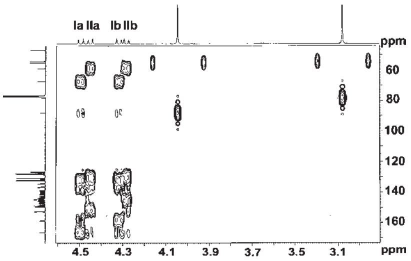


Figure 2. Expanded HMBC NMR spectrum of compound **5**.

The accurate MS of **5** (Figure S23) shows that the compound is a tetraadduct with a formula of $(C_6H_5CH_2)_2(CH_3O)_2C_{60}$, and the ^1H (Figure S19), ^{13}C (Figure S20), and HSQC (Figure S21) NMR of the compound are in good agreement with the formation of a tetraadduct. Figure 2 shows the HMBC NMR spectrum of **5**, which provides key data for structural elucidation. First, it shows that the two sets of methylene protons all have correlations with the most downfield resonance at 166.39 ppm, which are correlated via the $^3J_{CH}$ couplings, indicating that the two benzyls are both located next to this sp^2 C_{60} carbon; Second, the spectrum shows that the AB_q I (4.41 ppm) and the methoxyl protons (4.05 ppm) are both correlated with the resonance at 87.96 ppm, which is due to the sp^3 C_{60} carbon bonded to the methoxy group, indicating that the benzyl (AB_q I) and the methoxyl are positioned with a 1,2-configuration. In contrast, no correlation is shown between the AB_q II (4.38 ppm) and either one of the sp^3 $C_{60}{-}O$ carbons (78.08 or 87.96 ppm), indicating that this benzyl is likely to have a 1,4-addition pattern with respect to the two methoxy groups.

Since the two C_{60} sp^3 carbons that bonded to the two benzyls are connected to the same sp^2 C_{60} carbon, and one pair of methoxyl and benzyl groups is positioned with a 1,2-configuration, while the other benzyl is positioned with a 1,4-pattern relative to both methoxy functionalities, the only possible structure for the product is

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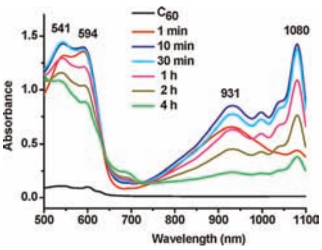


Figure 3. In situ visible–near-IR spectra for the reaction of C_{60} (5.0×10^{-4} M) with 5 equiv of CH_3O^- and 20 equiv of $PhCH_2Br$ at different reaction times in deoxygenated PhCN at 50 °C.

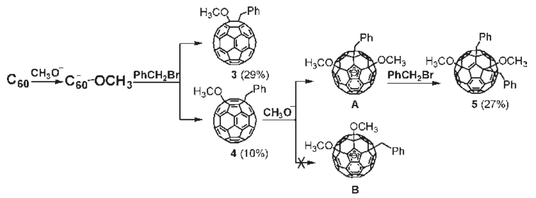
1,15-$(CH_3O)_2$-2,4-$(C_6H_5CH_2)_2C_{60}$. Such a configuration has been shown to be favorable for C_{60} tetraadducts involving both 1,2- and 1,4-additions, no matter if the products are formed via nucleophilic additions to electron-deficient C_{60}[8,9,11,16] or electrophilic additions to electron-rich anionic C_{60} species.[44]

Further study with 1,4- and 1,2-$(C_6H_5CH_2)(CH_3O)C_{60}$ shows that **5** can be obtained starting from 1,4-$(C_6H_5CH_2)(CH_3O)C_{60}$, while it cannot be obtained from the reaction starting from 1,2-$(C_6H_5CH_2)(CH_3O)C_{60}$ (Figures S24 and S25 for HPLC). The results are consistent with previous reports[8,9,11,16] and indicate that **5** is likely formed via an indenide intermediate monoanion ($R_3C_{60}^-$) as proposed by Nakamura et al.[8,9,11]

Figure 3 shows the in situ vis–near-IR spectrum of the nucleophilic additions of CH_3O^- to C_{60} in the presence of $PhCH_2Br$. A broad absorption band at 931 nm appears immediately after adding TBAOH/CH_3OH into C_{60} PhCN solution, in which $PhCH_2Br$ is present. The absorption band is essentially identical to that when no $PhCH_2Br$ is present (Figure 1), suggesting that this absorption is only related to the nucleophilic addition of RO^- ($R = H, CH_3$) to C_{60}. Unlike the case of OH^- addition, no shift occurs for the absorption band at 931 nm as the reaction proceeds, indicating any further change of the charged state for the resulting intermediate is unlikely. Absorption bands also appear at 594 and 541 nm, which are also different from those for dianionic intermediates as shown in Figure 1. The results indicate that the intermediates for the CH_3O^- addition to C_{60} are mostly monoanionic species, which are subsequently quenched with $PhCH_2Br$. In addition, an absorption band due to $C_{60}^{\bullet -}$ is also shown at 1080 nm, but with a much stronger intensity compared with the case of nucleophilic addition of OH^- to C_{60} (Figure 1), consistent with the presence of bulk monoanionic intermediates in the mixture.

Since the reaction is initiated with the formation of $CH_3OC_{60}^-$ as indicated by the in situ vis–near-IR spectrum, and no dimethoxy C_{60} compound is obtained, it implies that quenching of $CH_3OC_{60}^-$ with electrophiles is crucial for the reaction. The mechanism for the formation of **5** is proposed as shown in Scheme 2, where the reaction proceeds via an alternate nucleo- and electrophilic addition of CH_3O^- and $PhCH_2Br$.

Scheme 2. Proposed Mechanism for the Reaction of C_{60} with CH_3O^- and $PhCH_2Br$



The favorable formation of **5** as shown in the HPLC (Figure S17) indicates that the reaction of C_{60} with CH_3O^- and $PhCH_2Br$ prefers the formation of the symmetrical indenide intermediate **A** over the asymmetrical **B**. Computational calculations using Hatree–Fock (HF) methods at the 6-31G level with the Gaussian 03 program predict that **A** is favored over **B** by ~6.4 kcal/mol, which may be rationalized by the higher degree of conjugation of the 10 π-electron indenide anion of **A** compared to that of **B** (Figure S26) due to the higher symmetry of **A**, where the bond lengths of the indenide π-conjugation ring are more averaged compared to the case of **B**.

In summary, nucleophilic additions of OH^- and CH_3O^- to C_{60} are revisited, and well-structured oxygenated C_{60} derivatives have been isolated and characterized. The results show that OH^- functions as not only a nucleophile to react with C_{60} but also a base to depronate the C_{60}^-–OH intermediate and form the reactive C_{60}^-–O^- intermediate, which may further react with the nitrile via an anion relay mechanism to form fullerooxazolines; as for the nucleophilic addition of CH_3O^- to C_{60}, the results show that only monoanionic intermediates of $CH_3OC_{60}^-$ are produced during the reaction, and it is necessary to quench the monoanionic intermediates with electrophiles to obtain well-structured monomethoxylated and multiple methoxylated C_{60} derivatives. This work extends the scope of nucleophiles that are suitable for fullerene functionalizations and may shed light on developing new methods for preparing oxygenated fullerenes via direct nucleophilic reactions.

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Supporting Information Available. Experimental and calculation details, and spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.