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Aerobic Oxidations of C_{60}^{2-} in the Presence of PhCN and $PhCH_2CN$: Oxygenation versus Dehydrogenation Reactions

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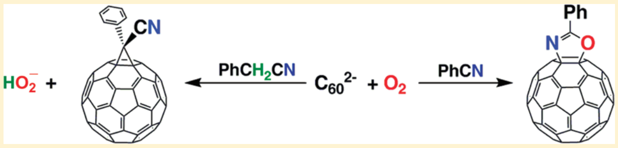
S Supporting Information

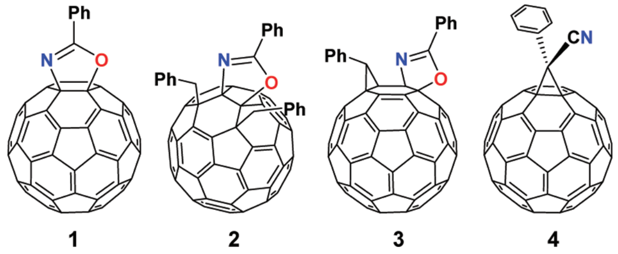
ABSTRACT: Aerobic oxidations of dianionic C_{60} were examined in PhCN and $PhCH_2CN$, where dioxygen was activated to $O_2^{\bullet-}$ via the single-electron transfer from C_{60}^{2-} and underwent oxygenation and dehydrogenation reactions, respectively. Addition of $PhCH_2Br$ led to further benzylation for the oxygenated product but not for the dehydrogenated one, suggesting that the initial two negative charges were preserved for the intermediates of the oxygenation reaction but not for those of the dehydrogenation reaction.



Carbanions are important reactive intermediates in organic synthesis.[1−3] Oxidation of such species with dioxygen leads to the formation of alcohols via a superoxide anion radical mechanism.[4] With the recent development of fullerene chemistry, it has been shown that fullerene anions, represented by C_{60}^{2-}, are an important class of carbanions that can be readily prepared and used as building blocks for fullerene functionalizations.[5−11] Similar to general carbanions, anionic fullerenes are sensitive to O_2 and are among the rare examples of non-metal catalysts capable of oxygen activation.[12−14] However, in most cases, the generated superoxide anion radical either evolved into reactive oxygen species (ROS) for DNA cleavage[12,13] or was involved in the reductive polymerization of anionic C_{60}.[15,16] Only in very limited cases has the activated oxygen been shown to undergo reactions with C_{60} to afford well-structured C_{60} derivatives,[17−19] which is quite unusual considering the rich chemistry of fullerenes.[20]

We have recently reported the synthesis of C_{60} oxazoline compounds (**1**, **2**, and **3** in Scheme 1) via the reaction involving trianionic C_{60} species and nitriles.[21,22] The reaction is intriguing since it shows a room-temperature attack of nitriles, which are typically inert and require harsh conditions for transformations. However, the origin of the oxygen atom still remains ambiguous, and the reaction mechanism has not been clarified.

Scheme 1. Structural Illustrations of Compounds 1−4



An alternative approach for conversion of C_{60} and nitriles into C_{60} oxazolines was achieved by Wang and co-workers with the use of $FeClO_4\cdot 6H_2O$ as both the catalyst and oxygen source,[23] where a much higher temperature was required compared to the reaction initiated by anionic C_{60}. Herein, we report the aerobic oxidations of C_{60}^{2-} in the presence of PhCN and $PhCH_2CN$. The results show that dioxygen is activated by C_{60}^{2-} via SET (single-electron transfer), and the generated $O_2^{\bullet-}$ undergoes either oxygenation for the formation of fullerene oxazolino heterocycles (**1** and **2**) or dehydrogenation reaction for methanofullerene (**4** in Scheme 1), depending on the structures of the nitriles.

Details of the aerobic oxidation of C_{60}^{2-} in PhCN are described in the Experimental Section. The crude products were partially soluble in toluene, and the soluble part was subjected to HPLC purification, while the insoluble part was likely due to the polymerization involving C_{60} epoxide species[15,16,24] and remained unidentified. HPLC (Figure S1 in Supporting Information) shows the formation of compound **1**, whose identity is confirmed by spectral characterizations in light of previous work.[21,23] The results show unambiguously that the oxygen atom for the C_{60} oxazolines obtained from trianionic C_{60} species is from dioxygen, consistent with the electrophilic nature of the oxygen atom exhibited during the reaction.[22] The fact that only C_{60}^{3-} could undergo the reaction while C_{60}^{2-} could not as observed previously[21,22] is likely due to the greater reactivity of C_{60}^{3-} compared with that C_{60}^{2-},[25,26] and the existence of only traces of dioxygen in the reaction system.

In situ cyclic voltammetry was performed to follow the reaction as shown in Figure 1. The most notable feature is the deformation of the cyclic voltammograms (CVs) of C_{60}^{2-} after addition of air (oxygen), indicating a reaction involving C_{60}^{2-}

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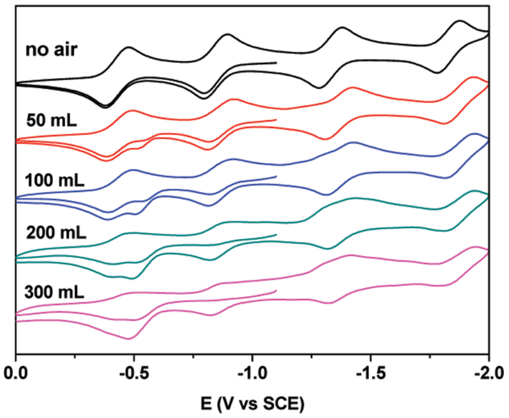


Figure 1. In situ CVs of 200 mg of dianionic C_{60} in 150 mL of PhCN solution containing 0.1 M TBAP with the addition of 0, 50, 100, 200, and 300 mL of air along with the flow of argon.

and O_2 occurred. An irreversible anodic wave appeared at −0.53 V vs SCE, which has been assigned to the singly bonded dianionic oxazolino C_{60} intermediate.[27] The irreversible anodic wave kept increasing as more air was introduced; however, the overall yield of the heterocyclic product might decrease due to the formation of more polymerized materials.

In order to have a better understanding of the reaction mechanism, $PhCH_2Br$ was added into the air-injected C_{60}^{2-}/PhCN system. Interestingly, *cis*-1 1,4-benzylated oxazolino C_{60} product (**2**) was obtained (Figure S2 in Supporting Information for HPLC), indicating that the initial two negative charges on C_{60} cage were preserved for the intermediates during the reaction. Since the $E_{1/2}$ values for the redox couples of $C_{60}^{\bullet-}/C_{60}^{2-}$ and $O_2/O_2^{\bullet-}$ are very close (−0.84 and −0.89 V vs SCE, Figure S3 in Supporting Information), it is likely that a SET occurs from C_{60}^{2-} to dioxygen to form $C_{60}^{\bullet-}$ and $O_2^{\bullet-}$.[15,16] Such an electron-transfer is enhanced especially when the generated $O_2^{\bullet-}$ is consumed in the subsequent reactions. The preservation of the two negative charges for the intermediates of the reaction implies that the generated $O_2^{\bullet-}$ would combine with $C_{60}^{\bullet-}$ via the radical coupling reaction during the subsequent steps with the formation of C_{60}^{-}-O_2^{-}.

The essential role of C_{60}^{2-} in the oxygenation reaction was demonstrated by the control reaction of $C_{60}^{\bullet-}$ with $O_2^{\bullet-}$ (KO_2 in 18-crown-6 ether) in PhCN, where most of the products were toluene-insoluble materials with no oxazolino product being obtained. The C_{60}^{-}-O_2^{-} is expected to form via the radical coupling reaction of $C_{60}^{\bullet-}$ with $O_2^{\bullet-}$; however, the critical reductive cleavage of the O−O bond is inhibited by the lack of C_{60}^{2-}, which hinders the formation of **1**.

To obtain a better understanding of the reaction involving C_{60}^{2-} and O_2, the reaction was performed with the introduction of benzyl cyanide ($PhCH_2CN$). Compared to PhCN, $PhCH_2CN$ has a much narrower electrochemical potential window (Figure S4 in Supporting Information), and the experiment was therefore carried out by first producing C_{60}^{2-} (90 mg) in PhCN (70 mL), followed by addition of 5 μL of $PhCH_2CN$ and injection of air, rather than being performed in neat $PhCH_2CN$ solution to avoid complications caused by possible electroreduction of $PhCH_2CN$. Surprisingly, no C_{60} oxazolino product was obtained. Instead, a dehydrogenated product, 1′-cyano-1′-phenyl-1,2-methano[60]fullerene (**4**) was produced (Figure S5a in Supporting Information for HPLC). The structure proof for compound **4** is given below, including an X-ray structure. Notably, C_{60} oxazolino product was obtained from the reaction of C_{60} with $PhCH_2CN$ and $FeClO_4 \cdot 6H_2O$,[23] indicating that the mechanisms for the nitrile activation by anionic C_{60} and $FeClO_4 \cdot 6H_2O$ are different. The absence of the oxygenated product for the aerobic oxidation of C_{60}^{2-} involving $PhCH_2CN$ was further confirmed as more $PhCH_2CN$ (90 μL) was used, where C_{60} multiple adducts were likely formed as judged by the shortened HPLC retention time (Figure S5b in Supporting Information). Notably, as the ^1H NMR of the crude reaction mixture (Figure S6 in Supporting Information) implies, there should be only dehydrogenated products formed since the resonances corresponding to the methylene protons of oxygenation products are missing.[23]

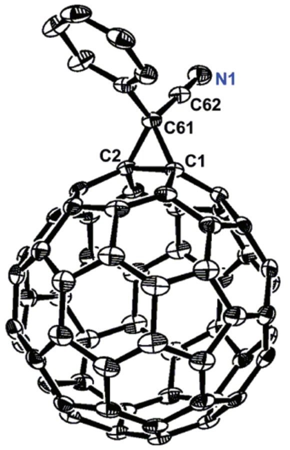


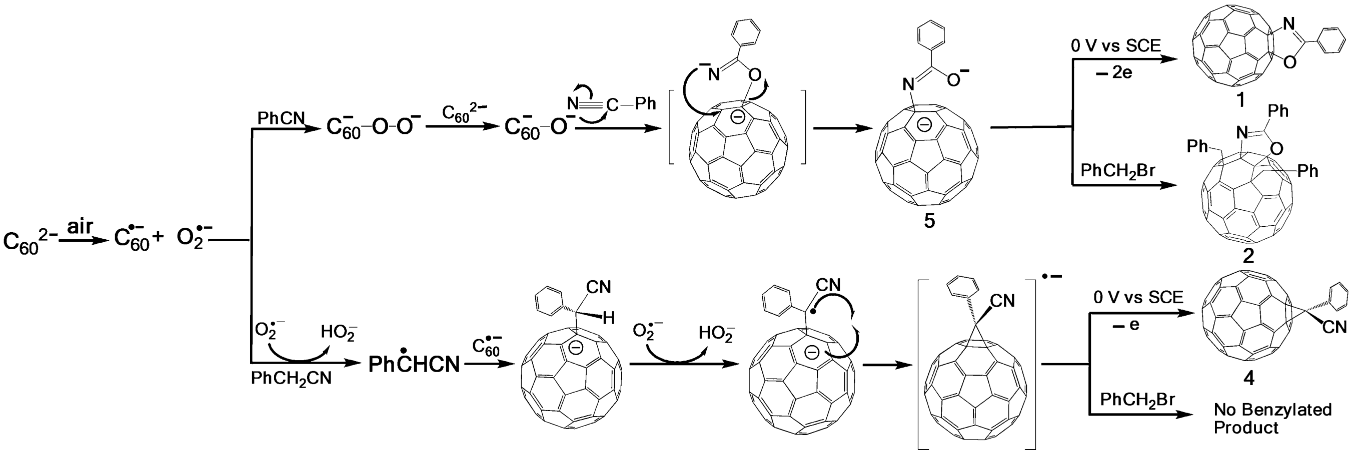
Figure 2. ORTEP diagram for **4** with 50% thermal ellipsoids. Hydrogen atoms and solvent molecules were omitted for clarity.

Figure 2 shows the X-ray single-crystal structure of compound **4** with partial atomic numbering. The methano functionality is clearly present. The C1−C2−C61 group forms a nearly equilateral triangle, with the bond lengths of C1−C2, C2−C61, and C61−C1 being 1.593(4), 1.520(3), and 1.517(3) Å, respectively. The most notable feature of the structure is the linear nature of C61−C62−N1 (177.7(3)°) and a distance of 1.142(3) Å for the C62−N1 bond length, which shows explicitly that the C≡N functionality in $PhCH_2CN$ is preserved in the reaction.

The structure of compound **4** is further supported by accurate MS, ^1H and ^{13}C NMR, and UV−vis characterizations (Figures S7−S10 in Supporting Information). The $[M + H]^+$ ($C_{68}H_6N^+$, calcd 836.04948) appears at 836.04878, and the $[M + Na]^+$ ($C_{68}H_5NNa^+$, calcd 858.03142) is shown at 858.03300 in the mass spectrum. In the ^1H NMR, the resonances corresponding to methylene protons are missing. A total of 27 resonances are seen for the sp^2 C_{60} carbons in the ^{13}C NMR, indicating that the compound has C_s symmetry, and the resonance corresponding to the cyano carbon atom appears at 114.8 ppm. As for the UV−vis spectrum, an absorption spike is shown at 426 nm, consistent with the characteristic absorption band for methanofullerenes.[28]

Benzylation experiment was also performed by adding $PhCH_2Br$ into the reaction mixture of C_{60}^{2-} with O_2 and $PhCH_2CN$ prior to oxidation. However, no benzylated product of compound **4** was obtained, indicating that the precursor of **4** is no longer a dianion, suggesting that the resulting $C_{60}^{\bullet-}$ and $O_2^{\bullet-}$ did not combine together after being generated during this reaction pathway. A reaction mechanism is therefore

Scheme 2. Proposed Mechanism for the Aerobic Oxidations of C_{60}^{2-} in the Presence of PhCN and $PhCH_2CN$[a]



[a]The negative charge is drawn in the hexagon of C_{60} for clarity. The negative charge should actually be delocalized over a much larger area of C_{60} due to π-conjugation.

proposed for the aerobic oxidation of C_{60}^{2-} in the presence of PhCN and $PhCH_2CN$ as shown in Scheme 2.

For both the oxygenation and dehydration reactions, the reactions were initiated by a SET between C_{60}^{2-} and O_2 to afford $C_{60}^{\bullet-}$ and $O_2^{\bullet-}$, which underwent a different pathway during the subsequent reaction steps. For the formation of compounds **1** and **2**, the resulting $C_{60}^{\bullet-}$ and $O_2^{\bullet-}$ formed C_{60}^{-}-O_2^{-} by a follow-up radical coupling reaction, which was also proposed to account for the electroreductive polymerization of C_{60} in the presence of dioxygen.[15,16] The combination of two negatively charged radical anions ($C_{60}^{\bullet-}$ and $O_2^{\bullet-}$) may seem unreasonable at the first sight; however, it is noteworthy that the unit negative charge on C_{60} is actually delocalized over the whole surface due to the π-conjugation of the molecule, where each individual carbon atom carries only 1/60 of the unit negative charge due to the π-conjugation of the molecule, which may greatly decrease the repulsion between the two negatively charged species. The O−O bond in C_{60}^{-}-O_2^{-} was then cleaved via reduction by C_{60}^{2-}, similar to the O−O cleavage mediated by Grignard reagent,[4] leading to the formation of the key intermediate C_{60}^{-}-O^{-}. The results indicate that the C_{60}^{-}-O^{-} is a strong oxygen nucleophile, capable of attacking the inert cyano group under ambient conditions, and forms anionic imine species. The anionic imine subsequently attacks C_{60}, accompanied by a heterolytic cleavage of the C_{60}−O bond, forming the dianionic precursor **5**, which is suggested to account for the irreversible anodic wave at −0.53 V vs SCE in CV.[27] Since the intermediate **5** retains two negative charges, it would lead to the formation of **2** upon addition of benzyl bromide or compound **1** upon oxidation. The assignment of $C_{60}O^{2-}$ as the nucleophile capable of attacking the cyano group under ambient conditions is reasonable, because $C_{60}O^{-}$ should be a weaker nucleophile than OH^{-} due to the strong electronegativity of C_{60}, while OH^{-} itself is unable to attack cyano group under mild conditions; as for C_{60}^{2-}, it is a weak nucleophile due to the delocalization of the charges over the C_{60} skeleton.[9] In addition to its unusual nucleophilicity, $C_{60}O^{2-}$ has been identified as the initiator for electroreductive polymerization of $C_{60}O$.[15,24] Notably, an alternative pathway of O−O cleavage was proposed via the oxidation of $C_{60}O_2^{2-}$ by C_{60},[16] leading to the formation of $C_{60}O^{-}$; however, such a pathway is unlikely for the current case since the generated $C_{60}O^{-}$ intermediate has only one negative charge and would therefore not be able to react with benzyl bromide during the subsequent steps, inconsistent with the experimental observations.

As for the aerobic oxidation of C_{60}^{2-} in the presence of $PhCH_2CN$, the generated superoxide anion radical would undergo dehydrogenation reaction rather than the oxygenation reaction due to the greater reactivity of the methylene protons. In this process, the resulting $O_2^{\bullet-}$ would first remove an H• to form PhCH•CN, which would then react with $C_{60}^{\bullet-}$ and produce the singly bonded $C_{61}HPhCN^{-}$ intermediate. The $O_2^{\bullet-}$ would then remove the remaining methine proton, followed by an intramolecular cyclization, and form the $C_{61}PhCN^{\bullet-}$ intermediate. Since the intermediate bears only one negative charge, it would not undergo the benzylation reaction with $PhCH_2Br$ and would produce compound **4** via oxidation. Control reaction of $C_{60}^{\bullet-}$ with $O_2^{\bullet-}$ (KO_2 in 18-crown-6 ether) and $PhCH_2CN$ led to the formation of compound **4**, indicating that no reductive cleavage of O−O by C_{60}^{2-} is required for the dehydrogenation pathway. Notably, the oxygenation reaction of PhCN is severely inhibited by the dehydrogenation reaction, even though there is much more PhCN than $PhCH_2CN$ (70 mL vs 5 μL).

The aerobic oxidation of C_{60}^{2-} was further examined with the use of $CH_3CH_2OOCCH_2CN$ and *m*-CH_3PhCN. No methanofullerene product was obtained when $CH_3CH_2OOCCH_2CN$ was used, confirming that the reaction of $O_2^{\bullet-}$ with the aliphatic protons takes place via the radical mechanism rather than the acid−base mechanism, since the methylene protons of $CH_3CH_2OOCCH_2CN$ are more acidic than the counterparts of $PhCH_2CN$ (pK_a = 13.1 vs pK_a = 21.9).[29,30] For both the $CH_3CH_2OOCCH_2CN$ and *m*-CH_3PhCN cases, a large amount of toluene-insoluble polymerized materials (≥80% weight) were produced, while much less oxazolino product was obtained for *m*-CH_3PhCN compared with the case when PhCN was used, and no oxazolino product was obtained for $CH_3CH_2OOCCH_2CN$. Such an outcome is likely due to the presence of aliphatic protons of the molecules, which produce radical species via the reaction of $O_2^{\bullet-}$, consistent with the results of $PhCH_2CN$.

Figure 3 shows the cyclic voltammogram of **4** at room temperature. Unlike previous results on the electrochemistry of

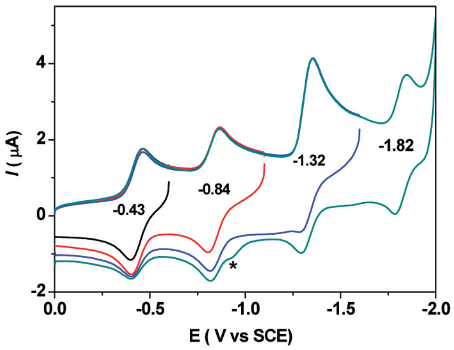


Figure 3. Cyclic voltammograms of compound **4** in PhCN containing 0.1 M TBAP with a scan rate of 0.1 V/s under Ar.

methanofullerenes bearing cyano groups, where the compounds showed decomposition upon reduction at room temperature,[31] compound **4** exhibits special electrochemical stability by showing two reversible one-electron transfer redox processes with $E_{1/2}$ at −0.43 and −0.84 V vs SCE, respectively, which are identical to those of C_{60}. As for the third reduction, the $E_{1/2}$ (−1.32 V vs SCE) is again almost identical to that of C_{60}, but the reducing current is unusually large, which is probably due to an unknown catalytic process, as observed previously for the third reduction of compound **2**.[32] As for the fourth reduction, it shows a reversible redox couple with $E_{1/2}$ at −1.82 V vs SCE. However, the compound may start to decompose after the fourth reduction, since a new oxidation wave labeled with an asterisk appears at −0.94 V as shown in Figure 3.

In summary, aerobic oxidations of C_{60}^{2-} in the presence of PhCN and $PhCH_2CN$ are reported, where oxygenation and dehydrogenation reactions take place with nitriles depending on their structures. A strong oxygen nucleophile C_{60}^{-}-O^{-} is proposed during the reaction of C_{60}^{2-} and O_2, which is capable of activating the C≡N bond under ambient conditions. On the other hand, dehydrogenation reaction is more favorable for $PhCH_2CN$ due to the presence of aliphatic protons, leading to the formation of methanofullerenes.

■ EXPERIMENTAL SECTION

General Methods. Tetra-*n*-butylammonium perchlorate (TBAP) was recrystallized from absolute ethanol and dried under vacuum at 313 K prior to use. All reactions were performed under argon atmosphere unless otherwise noted. Benzonitrile (PhCN) was distilled over P_2O_5 under vacuum at 305 K prior to use. All other reagents and solvents were obtained commercially and used as received. ^{1}H NMR spectra were recorded on 600 MHz spectrometer, and ^{13}C NMR spectra were recorded on 150 MHz spectrometer. MALDI (matrix-assisted laser desorption ionization) mass spectrum was acquired using a MALDI-TOF mass spectrometer equipped with a nitrogen laser. Accurate MS measurement was performed using an ESI electrospray ionization Fourier transform ion cyclotron resonance mass spectrometer (ESI FT-ICR MS).

Controlled-potential bulk electrolysis was carried out on a potentiostat/galvanostat using an "H" type cell that consisted of two platinum gauze electrodes (working and counter electrodes) separated by a sintered glass frit. A three-electrode cell was used for CV measurements and a glassy carbon, a platinum, and a saturated calomel electrode (SCE) were used as working electrode, counter electrode, and reference electrode, respectively. A fritted-glass bridge of low porosity which contained the solvent/supporting electrolyte mixture was used to separate the SCE from the bulk of the solution.

Aerobic Oxidation of C_{60}^{2-} in PhCN Followed by Electrochemical Oxidation. Typically, 200 mg (277.8 μmol) of C_{60} in 150 mL of freshly distilled PhCN solution containing 0.1 M TBAP was electroreduced at −1.10 V vs SCE under Ar atmosphere. The potentiostat was switched off once the theoretical number of electrons required for reducing C_{60} to C_{60}^{2-} was achieved to avoid the production of C_{60}^{3-}. The generated C_{60}^{2-} was exposed to oxygen by injecting 100 mL of air (molar ratio $C_{60}/O_2 \approx 1{:}3$) along with the flow of Ar. The color of the solution changed immediately from red to green. The reaction mixture was then oxidized electrochemically back to neutral with a potential of 0 V vs SCE. The solvent was removed under reduced pressure, and the residue was washed with methanol to remove TBAP. The obtained crude product was purified using a Buckyprep HPLC column eluted with toluene at a flow rate of 3.7 mL/min and the detector wavelength set at 380 nm. Compound **1** was obtained with a yield of 18% (43 mg) along with 55 mg of unreacted C_{60}. The rest of the reaction mixture was insoluble in toluene or CS_2 and was likely due to the polymerization reaction involving C_{60} epoxide species. The spectral data for **1** are in good agreement with previous results. Spectral data for **1**: MALDI FOT-MS, *m*/*z* calcd for $C_{67}H_5NO$ $[M + H]^+$ 840.04, found 840.04; ^{1}H NMR (600 MHz, in $CS_2/CDCl_3$ solvent) δ ppm, 8.42 (*d*, 2H), 7.66 (*t*, 1H), 7.60 (*t*, 2H); ^{13}C NMR (150 MHz, CS_2, DMSO-d_6 as the external lock solvent) δ ppm, 164.3 (1C, C=N), 147.5 (2C), 147.1 (1C), 145.7 (4C), 145.5 (2C), 145.4 (2C), 145.3 (2C), 145.1 (2C), 145.0 (2C), 144.8 (2C), 144.5 (2C), 144.4 (2C), 144.2(2C), 143.9 (2C), 143.6 (2C), 143.0 (2C), 142.1 (2C), 142.1 (2C), 142.0 (2C), 141.7 (4C), 141.6 (2C), 141.4 (2C), 141.3 (4C), 139.8 (2C), 138.9 (2C), 137.2 (2C), 136.6(1C), 135.4 (2C), 131.7 (1 C, Ph), 128.7 (2C, Ph), 128.1 (2C, Ph), 126.4 (1C, Ph), 96.6 (1C, sp^3, C−O), 91.6 (1C, sp^3, C−N).

Aerobic Oxidation of C_{60}^{2-} in PhCN Followed by Quenching with $PhCH_2Br$. Procedures for the generation and dioxygen oxidation of C_{60}^{2-} are identical to those described above. After introduction of O_2, 100-fold $PhCH_2Br$ was added to the system. The benzylation reaction was allowed to proceed for 3 h under Ar. The obtained crude product was purified by HPLC, and the workups for purifications were similar to those where the mixture was electrochemically oxidized back to neutral. Starting with 200 mg C_{60}, compound **2** was obtained with a 16% yield (45 mg), along with small amount of 1,4-$(PhCH_2)_2C_{60}$ (4 mg), compound **1** (5 mg), and unreacted C_{60} (3 mg). The rest of the reaction mixture was insoluble in toluene or CS_2 and was likely due to the polymerization reaction involving C_{60} epoxide species. The spectral data for **2** are in good agreement with previous results. Spectral data for **2**: MALDI FOT-MS, *m*/*z* calcd for $C_{81}H_{19}NO$ $[M + H]^+$ 1022.2, found 1022.2; ^{1}H NMR(600 MHz, in CS_2, DMSO-d_6 as the external lock solvent) δ ppm, 8.13 (*d*, 2H), 7.40 (*t*, 1H), 7.36 (*t*, 2H), 7.11 (*d*, 4H), 6.97−6.79 (*m*, 6H), 4.11 (AB$_q$, $\Delta\nu_{AB}$ = 324 Hz, J_{AB} = 12 Hz), 4.06 (AB$_q$, $\Delta\nu_{AB}$ = 258 Hz, J_{AB} = 12 Hz); ^{13}C NMR (150 MHz, CS_2, DMSO-d_6 as the external lock solvent) δ ppm, 161.6 (1C, C=N), 152.6 (1C), 152.4 (1C), 148.7 (1C), 148.5 (1C), 148.4 (1C), 148.2 (1C), 147.5 (1C), 146.6 (1C), 146.6 (2C), 146.5 (2C), 146.3 (1C), 145.9 (1C), 145.6 (1C), 145.5 (2C), 144.9 (2C), 144.8 (1C), 144.7 (1C), 144.7 (1C), 144.6 (1C), 144.2 (1C), 144.2 (1C), 144.0 (2C), 143.8 (1C), 143.8 (2C), 143.7 (2C), 143.4 (2C), 143.3 (1C), 143.0 (1C), 142.9 (1C), 142.8 (1C), 142.6 (1C), 142.4 (1C), 142.3 (1C), 142.2 (1C), 142.0 (1C), 141.7 (1C), 141.6 (1C), 141.3 (1C), 141.2 (2C), 141.0 (1C), 139.3 (1C), 139.0 (1C), 138.9 (1C), 137.6 (1C), 136.8 (1C), 136.4 (1C), 135.9 (1C), 135.8 (1C), 134.5 (1C, Ph), 134.2 (1C, Ph), 133.7 (1C, Ph), 131.5 (1C, Ph), 131.5 (1C, Ph), 131.3 (1C, Ph), 128.3 (2C, Ph), 128.2 (2C, Ph), 127.6 (1C, Ph), 127.5 (2C, Ph), 127.4 (2C, Ph), 127.3 (1C, Ph), 126.6 (1C, Ph), 126.3 (1C, Ph), 97.1 (1C, sp^3, C−O), 90.8 (1C, sp^3, C−N), 62.2 (1C, sp^3, C−CH_2Ph), 61.2 (1C, sp^3, C−CH_2Ph), 46.2 (1C, CH_2), 45.3 (1C, CH_2).

Aerobic Oxidation of C_{60}^{2-} in the Presence of $PhCH_2CN$. Because $PhCH_2CN$ starts to be reduced around −0.8 V vs SCE, the aerobic oxidation of C_{60}^{2-} was performed by first generating C_{60}^{2-} in PhCN, followed by adding a small amount of $PhCH_2CN$ along with O_2 to avoid the electroreduction of $PhCH_2CN$. Typically, 90 mg of C_{60} (125 μmol) was electrolyzed with a potential of −1.10 V vs SCE under Ar in 70 mL of 0.1 M TBAP PhCN solution. The potentiostat was switched off once the theoretical number of electrons required for reducing C_{60} to C_{60}^{2-} was achieved to avoid the production of C_{60}^{3-}.

Then 5 μL of $PhCH_2CN$ was added to the solution, followed by injecting 150 mL of air (molar ratio $C_{60}/O_2 \approx 1:11$) along with the flow of Ar. The reaction mixture was then oxidized electrochemically back to neutral with a potential of 0 V vs SCE, and the crude product was purified using a Buckyprep HPLC column eluted with toluene. Compound **4** was obtained with 16% yield (17 mg), along with 21 mg of unreacted C_{60}. Spectral data for **4**: positive ESI FT-ICR MS, *m*/*z* calcd for $C_{68}H_6N^+$ $[M + H]^+$ 836.04948, found 836.04878; calcd for $C_{68}H_5NNa^+$ $[M + Na]^+$ 858.03142, found 858.03300; UV−vis (hexane) λ_{max} 255, 325, and 426 nm; ^{1}H NMR (600 MHz, in $CS_2/CDCl_3$) δ ppm, 8.02 (d, 2H), 7.60 (m, 3H); ^{13}C NMR (150 MHz, $CS_2/CDCl_3$) δ ppm, 145.2 (2C), 145.1 (2C), 145.1 (4C), 144.8 (4C), 144.7 (2C), 144.7 (2C), 144.6 (4C), 144.5 (2C), 144.4 (2C), 144.3 (1C), 144.2 (2C), 144.0 (1C), 143.7(2C), 143.5(2C), 142.9(2C), 142.8(2C), 142.8 (2C), 142.7 (3C), 142.7(1C), 142.2 (2C), 141.9 (2C), 141.8 (2C), 141.5 (2C), 141.1 (2C), 140.8 (2C), 138.8 (2C), 138.7 (2C), 131.6 (2C, Ph), 130.0 (1C, Ph), 129.1 (2C, Ph), 128.7 (1C, Ph), 114.8 (1C, sp^3, C≡N), 71.9 (2C, sp^3), 36.7 (1C, $\mathrm{Ph\underline{C}CN}$) .

X-ray Single-Crystal Diffraction of 4. Black crystals of **4** were obtained by slowly diffusing hexane into a CS_2 solution of **4** at room temperature. Single-crystal X-ray diffraction data were collected on an instrument equipped with a CCD area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) in the scan range 1.37° < θ < 26.14°. The structure was solved with the direct method of SHELXS-97 and refined with full-matrix least-squares techniques using the SHELXL-97 program within WINGX. Crystal data of $4 \cdot 2CS_2$: $C_{69}H_5NOS_4$, $M_w = 975.98$, triclinic, space group *P*-1, *a* = 9.9728(8) Å, *b* = 13.2397(10) Å, *c* = 15.0024(11) Å, α = 93.1580(10)°, β = 97.3430(10)°, γ = 104.5030(10)°, *V* = 1894.2(3) Å^3, *Z* = 2, D_{calcd} = 1.711 Mg m^{-3}, μ = 0.311 mm^{-1}, *T* = 191(2) K, crystal size 0.12 × 0.16 × 0.09 mm^3; reflections collected 10619, independent reflections 7418; 4493 with $I > 2\sigma(I)$; *R*1 = 0.0557 $[I > 2\sigma(I)]$, w*R*2 = 0.1562$[I > 2\sigma(I)]$; *R*1 = 0.0730 (all data), w*R*2 = 0.1724 (all data), GOF (on F^2) = 1.063.

Control Reaction of $C_{60}^{\bullet-}$ with KO_2 in PhCN. $C_{60}^{\bullet-}$ (90 mg) was first generated by electrolysis at a potential of −0.60 V vs SCE in 0.1 M TBAP PhCN solution (70 mL). The potentiostat was switched off once the reduction was complete. One-fold of KO_2 (9 mg) dissolved in 18-crown-6 ether (132 mg, KO_2/ether = 1:4 molar ratio) was then put into the C_{60}^-/PhCN solution. The reaction mixture was then oxidized electrochemically back to neutral with a potential of 0 V vs SCE. Almost all of the crude product was insoluble in toluene or CS_2, and no oxazoline compound was obtained.

Control Reaction of $C_{60}^{\bullet-}$ with KO_2 in the Presence of $PhCH_2CN$. $C_{60}^{\bullet-}$ (90 mg) was first generated by electrolysis at a potential of −0.60 V vs SCE in 0.1 M TBAP PhCN solution (70 mL). The potentiostat was switched off once the reduction was complete. One-fold of KO_2 (9 mg) dissolved in 18-crown-6 ether (132 mg, KO_2/ether = 1:4 molar ratio) was then put into the C_{60}^-/PhCN solution along with 5 μL of $PhCH_2CN$. The reaction mixture was then oxidized electrochemically back to neutral with a potential of 0 V vs SCE. Compound **4** was obtained with a yield of 8% (8 mg), along with unreacted C_{60} (5 mg).

Aerobic Oxidation of C_{60}^{2-} in the Presence of $CH_3CH_2OOCCH_2CN$. Because C_{60} is insoluble in $CH_3CH_2OOCCH_2CN$, the procedures for the experiment were similar to those when $PhCH_2CN$ was used, i.e., the generation of C_{60}^{2-} was first carried out in PhCN, and 5 μL of $CH_3CH_2OOCCH_2CN$ was added into the system along with 150 mL of air. Most of the reaction product was toluene-insoluble materials, and no oxazoline or methanofullerene product was obtained.

Aerobic Oxidation of C_{60}^{2-} in the Presence of *m*-CH_3PhCN . The procedures were similar to those when PhCN was used, except *m*-CH_3PhCN was used instead of PhCN. Most of the reaction product was toluene-insoluble materials. Starting with 100 mg of C_{60}, only 3 mg of oxazoline product was obtained, along with 11 mg of recovered C_{60}.

ASSOCIATED CONTENT

Supporting Information

X-ray single-crystal crystallographic file for **4** in CIF format; CVs of C_{60} and O_2, HPLC traces, and copies of accurate MS, ^{1}H and ^{13}C NMR, and UV−vis spectral characterizations of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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