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Reaction of C_{60} with Diacyl Peroxides Containing Perfluoroalkyl Groups. The First Example of Electron Transfer Reaction *via* $C_{60}^{+\bullet}$ in Solution

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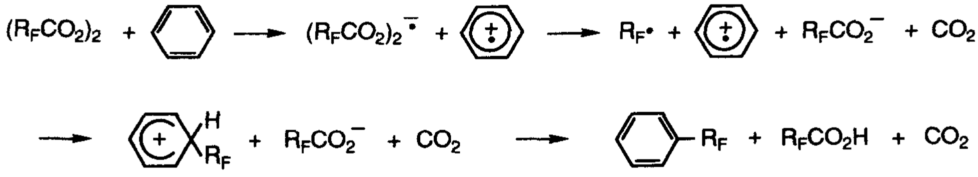
Abstract: The reaction of C_{60} with $(R_FCO_2)_2$ yielded $C_{60}(R_FOH)$ and $C_{60}(R_FCO_3H)$. The former was produced by single-electron transfer from C_{60} to the peroxide, and the latter by ionic or concerted addition of O-O bond in $(R_FCO_2)_2$ to C_{60}. The formation of $C_{60}(R_FOH)$ involves the cation radical of C_{60} as intermediate.

Buckminsterfullerene, C_{60}, is known to possess considerably high electron affinity and low ionization potential on the basis of both experimental measurements and theoretical calculations.[1] Thus, C_{60} can be reduced to afford $C_{60}^{-\bullet}$ easily and also oxidized to yield $C_{60}^{+\bullet}$ smoothly. In fact, chemical and electrochemical reductions of C_{60} have been extensively studied to give a series of anions ($C_{60}^{-\bullet}$ to C_{60}^{6-}),[2] and the single-electron transfer from organic molecule to C_{60} occurs smoothly to give the cation radical of organic molecules and $C_{60}^{-\bullet}$ corresponding to the high electron affinity of C_{60}.[3] However, oxidation of C_{60} in solution has proved rather difficult in spite of its low ionization potential,[4] and the cationic species $C_{60}^{+\bullet}$ has hardly employed for the organic synthesis. We now report here the first example of the single-electron transfer reaction from C_{60} to organic molecules in solution.

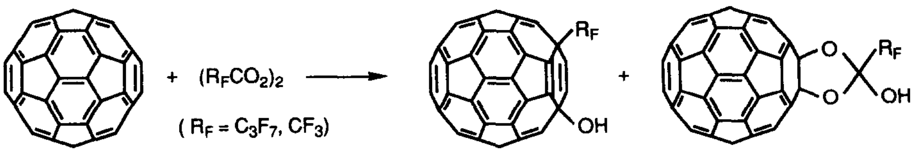
$$C_{60}^{\bullet-} \xleftarrow{\ e\ } C_{60} \xrightarrow{\ -e\ } C_{60}^{\bullet+}$$

Previously, we reported the single-electron transfer reaction of aromatic compounds to diacyl peroxides containing perfluoroalkyl groups.[5] Thus, the reaction of substituted benzenes with bis(perfluoroalkanoyl) peroxides produces perfluoroalkylbenzenes *via* perfluoroalkyl radicals shown in Scheme 1. Since the reaction involves the decarboxylation of bis(perfluoroalkanoyl) peroxides, electron transfer process in this reaction can be recognized exactly by detecting the products of cation radicals with perfluoroalkyl radicals. On the basis of this idea, we investigated the reactions of C_{60} with bis(perfluoroalkanoyl) peroxides.



Scheme 1

Treatment of C_{60} with bis(heptafluorobutylyl) peroxide[6] and bis(trifluoroacetyl) peroxide[5] in chlorobenzene at 40 °C under degassed conditions for 15 h gave two products [(**1** (25%) and **2** (11%), and **3** (10%) and **4** (31%), respectively], which can be separated by column chromatography on silica gel, followed by HPLC using gel permeation columns.[7]



1: $R_F = C_3F_7$
3: $R_F = CF_3$

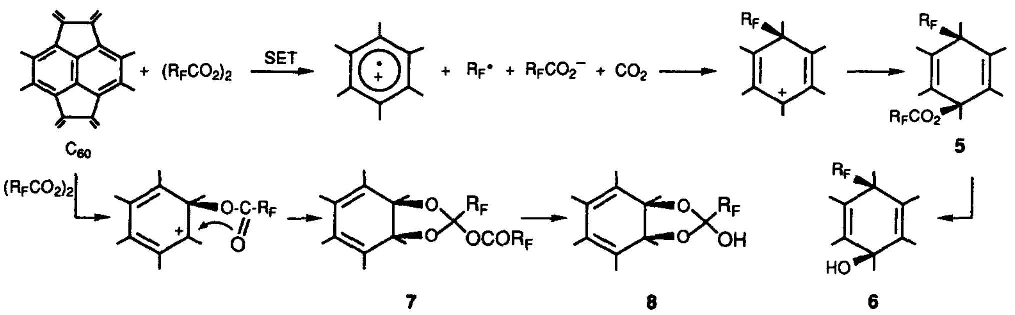
2: $R_F = C_3F_7$
4: $R_F = CF_3$

In the case of C_{60} with $(C_3F_7CO_2)_2$, the structure of the major product **1** was estimated by ^{13}C and ^{19}F NMR, IR, FAB mass, and UV-vis spectra.[8] FAB mass spectrometry of **1** ($C_{63}F_7HO$) clearly indicates a peak at 906 for adduct of C_3F_7 and hydroxyl groups. The ^{19}F NMR spectrum of **1** shows two singlets and an AB-type quartet (J = 265.5 Hz) for heptafluoropropyl group. Coupling constant of geminal fluorines is usually 160 Hz, whereas vicinal fluorines display no ^{19}F-^{19}F coupling. Therefore, two fluorines of the CF_2 group attached to the C_{60} moiety are unequivalent reflecting the unsymmetrical structure of **1**. The ^{13}C NMR spectrum of **1** shows 47 signals for the C_{60} skeleton: two carbons at δ 59.06 and 75.68 and the remainder between 138 and 151 . The signal at δ 59.06 displays triplet due to the coupling with CF_2 and is assigned to the carbon of C_{60} attached to CF_2. The signal at δ 75.68 (s) is situated in a position of the C_{60} carbon attached to the hydroxy group. It is worth noting that the C_{60} carbon attached to the fluoroalkyl group in **1** can be easily assigned by using the ^{13}C-^{19}F coupling. The structural analysis of the minor product **2** was carried out by comparison of the spectroscopic data[9] with the known C_{60} derivatives.[10] Although **2** has a unique orthoester part, **2** is stable enough under the conditions of isolation and spectroscopic measurements. The FAB mass spectrum of **2** shows the molecular ion peak at 950 (C_{60} + $C_4F_7HO_3$). The ^{19}F NMR spectrum of **2** shows three singlets of heptafluoropropyl group, and the ^{13}C NMR spectrum displays 25 signals corresponding to the C_{2v} structure.

In the reaction of C_{60} with $(CF_3CO_2)_2$, the products were characterized by comparison with **1** and **2**.[11] Thus, the reaction of C_{60} with diacyl peroxides containing perfluoroalkyl groups produces two types of products, and the reaction mechanisms can be explained by considering two pathways (Scheme 2). The first one contains the single-electron transfer from C_{60} to diacyl peroxide $(R_FCO_2)_2$ to produce $C_{60}^{+\bullet}$ and

$(R_FCO_2)_2^{-\bullet}$ which readily decomposes to $R_F^\bullet$, $R_FCO_2^-$, and CO_2. The radical coupling of $C_{60}^{+\bullet}$ with $R_F^\bullet$, followed by addition of $R_FCO_2^-$ results in the formation of **5**. The product **6** is formed by hydrolysis of **5** during the work-up. The another reaction pathway for **8** may involve the addition of $R_FCO_2^+$ to C_{60} to give $R_FCO_2\text{-}C_{60}^+$. Intramolecular cyclization of $R_FCO_2\text{-}C_{60}^+$, followed by addition of $R_FCO_2^-$ produces **7** which may be hydrolyzed to give **8**. For the formation of **8**, the concerted (simultaneous) addition of $(R_FCO_2)_2$ to C_{60} cannot be ruled out, and the resulting 1,2-diacetate may be hydrolyzed to give **8**.

We showed here the first single-electron transfer reaction from C_{60} to organic molecules under synthetic conditions. The other applications of the single-electron transfer for C_{60} chemistry are now under investigation.



Scheme 2

References and Notes

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7. Besides these two products, small amounts of the recovered C_{60} and unidentified C_{60} derivatives were obtained.
8. Spectral data of **1**: ^{13}C NMR(CS_2:CD_2Cl_2 = 5:1) δ 59.06(t, J_{CCF}=26.7Hz), 75.68, 138.87, 138.94, 139.11, 140.61, 141.69, 142.20, 142.58, 142.69, 142.89, 143.40, 143.48, 143.57, 143.64, 143.68, 143.75, 143.79, 143.92, 143.97, 144.01, 144.08, 144.14, 144.34, 144.37, 144.43, 144.68, 144.72, 144.79, 145.16, 145.65, 145.96, 146.15, 146.20, 146.26, 146.77, 147.10, 147.14, 147.34, 147.39, 147.56, 148.10, 148.47, 149.22, 149.28, 149.99, 150.79; ^{19}F NMR(CS_2:CD_2Cl_2 = 5:1, from ex. CF_3CO_2H) δ -46.03 (s, 2F), -35.54 (d, J=265.5Hz, 1F), -32.28 (d, J=265.5Hz, 1F), -4.96(s, 3F); IR (KBr) 1338, 1229, 1181, 1123, 1026, 849, 737, 673, 639, 585, 527, 475 cm^{-1}; UV-vis (toluene) λ_{max} = 444, 688 nm; FAB-MS (Pos., *m*-nitrobenzyl alcohol) m/z 907, 906(M$^+$), 889, 720.
9. Spectral data of **2**: ^{13}C NMR(CS_2:CD_2Cl_2 = 5:1) δ 95.56, 116.03(t, J_{CCF}=28.5Hz), 138.08, 138.89, 140.00, 140.04, 142.11, 142.14, 142.44, 142.51, 142.62, 142.67, 142.98, 143.13, 144.67, 144.78, 144.90, 144.94, 145.40, 145.43, 145.47, 145.53, 146.53, 146.82, 146.88, 148.67; ^{19}F NMR (CS_2:CD_2Cl_2 = 5:1, from ex. CF_3CO_2H) δ -49.30(s, 2F), -46.84(s, 2F), 5.46(s, 3F); IR (KBr) 1229, 1208, 1130, 990, 891, 743, 637, 527, 480, 440 cm^{-1}; UV-vis (toluene) λ_{max} 324, 682 nm; FAB-MS (Pos., *m*-nitrobenzyl alcohol) m/z 950 (M$^+$), 720.
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11. Spectral data of **3**: ^{13}C NMR (CS_2:CD_2Cl_2 = 5:1) δ 75.76, 138.94, 139.25, 141.80, 142.47, 142.53, 142.71, 142.82, 142.89, 143.48, 143.66, 143.70, 143.79, 143.92, 144.10, 144.23, 144.28, 144.36, 144.52, 144.56, 144.72, 144.79, 145.16, 145.47, 145.89, 145.95, 146.06, 146.09, 146.22, 146.81, 147.12, 147.32, 147.39, 147.54, 147.57, 148.34, 148.74, 149.22, 149.31, 150.23, 150.68; ^{19}F NMR (CS_2:CD_2Cl_2 = 5:1, from ex. CF_3CO_2H) δ 5.67 (s, 3F); IR (KBr) 1429, 1256, 1184, 1092, 1028, 984, 673, 639, 567, 529, 477 cm^{-1}; UV-vis (toluene) λmax 440, 690 nm; FAB-MS (Pos., *m*-nitrobenzyl alcohol) m/z 807 (M$^+$+1), 720.

    Spectral data of **4**: ^{13}C NMR (CS_2:CD_2Cl_2 = 5:1) δ 95.58, 114.74(q, J_{CCF}=38.6Hz), 138.14, 138.81, 140.02, 142.12, 142.18, 142.44, 142.51, 142.62, 142.67, 142.98, 143.13, 144.70, 144.78, 144.94, 145.43, 145.47, 145.78, 146.53, 146.79, 146.82, 146.86, 147.01, 148.67; ^{19}F NMR (CS_2:CD_2Cl_2 = 5:1, from ex. CF_3CO_2H) δ -8.53 (s, 3F); IR (KBr) 1428, 1190, 1138, 1184, 1059, 988, 783, 741, 675, 575, 525 cm^{-1}; UV-vis (toluene) λ_{max} 323, 685 nm; FAB-MS (Pos., *m*-nitrobenzyl alcohol) m/z 851 (M$^+$+1), 720.

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