

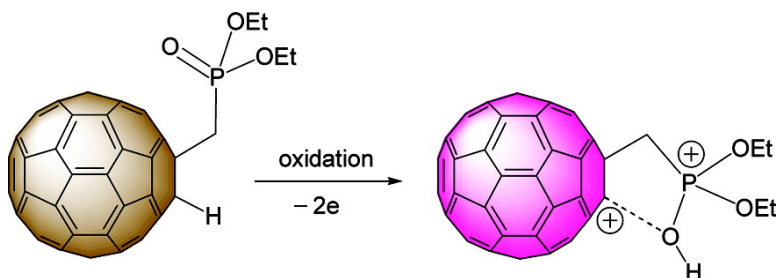
Communication

**Generation of Fullerenyl Cation (EtO)P(OH)CH-C
 from RC-H and from RC-CR (R = CHP(O)(OEt))**

Yasujiro Murata, Fuyong Cheng, Toshikazu Kitagawa, and Koichi Komatsu

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Generation of Fullerenyl Cation $(\text{EtO})_2\text{P}^+(\text{OH})\text{CH}_2\text{-C}_{60}^+$ from $\text{RC}_{60}\text{-H}$ and from $\text{RC}_{60}\text{-C}_{60}\text{R}$ ($\text{R} = \text{CH}_2\text{P}(\text{O})(\text{OEt})_2$)

Yasujiro Murata, Fuyong Cheng, Toshikazu Kitagawa, and Koichi Komatsu*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Received April 30, 2004; E-mail: komatsu@scl.kyoto-u.ac.jp

It is now generally accepted that fullerenes are typically electronegative molecules, and studies on their cationic species are quite limited.^{1,2} Thus, there have so far been reported only two methods for the generation of monofunctionalized C_{60} cations as stable species;^{3,4} RC_{60}^+ ($\text{R} = \text{CHCl}_2$ or $\text{CCl}_2\text{CH}_2\text{Cl}$) was generated by ionization of the corresponding monohydroxylic C_{60} (fullerenol) in a strong acid such as $\text{CF}_3\text{SO}_3\text{H}$,³ and HC_{60}^+ was formed by direct protonation of C_{60} by an extraordinarily strong superacid having a carborane structure.⁴ However, fullerenol is still a rather rare material⁵ and the latter superacid is not commonly available. The fullerenyl cation will become a more common and widely applicable species if monofunctionalized hydrofullerenes, $\text{RC}_{60}\text{-H}$, which can be synthesized by a variety of reactions,⁶ can be used as the precursor for the cation RC_{60}^+ . Here we report the first example of the generation of a fullerenyl cation, $(\text{EtO})_2\text{P}^+(\text{OH})\text{CH}_2\text{-C}_{60}^+$, from $\text{RC}_{60}\text{-H}$ ⁷ and also from $\text{RC}_{60}\text{-C}_{60}\text{R}$ ($\text{R} = \text{CH}_2\text{P}(\text{O})(\text{OEt})_2$)⁸ as precursors.

When $\text{RC}_{60}\text{-H}$ (**2**)⁷ was simply dissolved in H_2SO_4 at room temperature under air, a reddish purple solution was immediately formed. The ^1H NMR spectrum (D_2SO_4) showed that a single species was produced with disappearance of a signal for the proton originally attached to the C_{60} cage in **2**. As shown in Figure 1a, the UV-vis-NIR spectrum (H_2SO_4) showed absorptions at 488 nm ($\log \epsilon$ 3.75), 795 (3.42), and ~ 1122 (2.80), which are characteristic to the monofunctionalized C_{60} cations,^{3,4} the molar absorption coefficients being comparable to the reported values.³ Quenching this solution with $\text{CF}_3\text{CH}_2\text{OH}$ (TFE) afforded fullerenyl ether $\text{RC}_{60}\text{-OCH}_2\text{CF}_3$ in 85% isolated yield as a mixture of 1,2- and 1,4-isomers (**4** and **5**, respectively) in a ratio of 4:1. These findings indicate the nearly quantitative formation of a fullerenyl cation from **2** (Scheme 1). In exactly the same way, the same cationic species was generated quantitatively from singly-bonded fullerene dimer **3**.

The ^{13}C NMR spectrum ($\text{H}_2\text{SO}_4\text{-CF}_3\text{SO}_3\text{H}$ (1:4)) of the cationic species showed 29 signals in the region between 152.05 and 136.28 ppm in addition to a signal at 53.66 ppm for the sp^3 carbon on the C_{60} cage (Figure 1b), indicating C_s symmetry in this species. The cationic center exhibited a signal at 174.67 ppm, which is close to the reported ones (175.6 ppm for $\text{CHCl}_2\text{-C}_{60}^+$ and 174.9 ppm for $\text{CH}_2\text{ClCCl}_2\text{-C}_{60}^+$).³ This signal appeared as a doublet, which should be due to a coupling with the phosphorus atom ($J_{\text{P-C}} = 6.6$ Hz), whereas the corresponding carbon in **2** showed no such coupling.⁷ Thus, it was suggested that an oxygen atom in the phosphoryl group is coordinated to the cationic center to form a five-membered cyclic structure such as **A** in Figure 2. In support of this, the ^{31}P NMR spectrum (D_2SO_4) of this cationic species exhibited a signal at 31.08 ppm, which is downfield shifted by 7 ppm as compared with that of **2**, indicative of the presence of some positive charge on the phosphorus atom.

The structure of the cationic species was investigated by DFT calculations, particularly with regard to the possible coordination

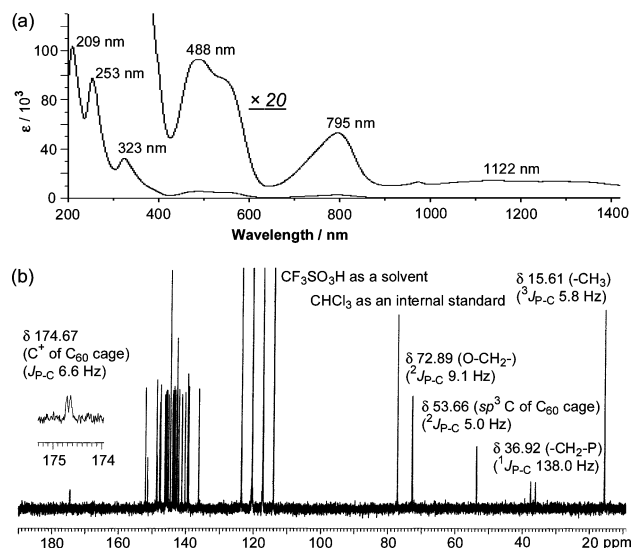
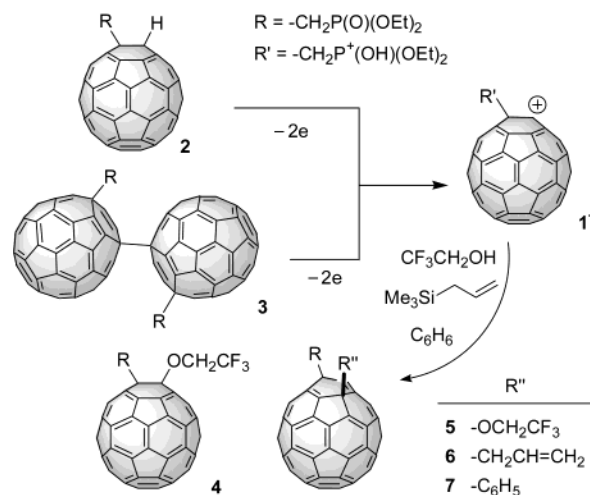


Figure 1. (a) UV-vis-NIR spectrum in H_2SO_4 and (b) the ^{13}C NMR spectrum in $\text{H}_2\text{SO}_4\text{-CF}_3\text{SO}_3\text{H}$ (1:4) of the cationic species.

Scheme 1



of the phosphoryl group to the cationic center as well as the conformation of the phosphorylmethyl group (structures **A-C** in Figure 2), in H_2SO_4 using the Onsager model.^{9,10} Although **A** was calculated to be more stable than **B** and **C** by 12.4 and 13.0 kcal mol^{-1} , respectively, the calculated chemical shift of **C2** in **A** (116.88 ppm) obtained by the GIAO method^{11,12} was completely different from the experimental value (174.67 ppm). Since the protonation on a phosphoryl oxygen is quite possible in a strongly acidic medium,¹³ we next examined the structures formed by protonation on **A-C**. The calculations using either **A** or **B** as an initial geometry with protonation on the phosphoryl oxygen gave **D** as an energy-

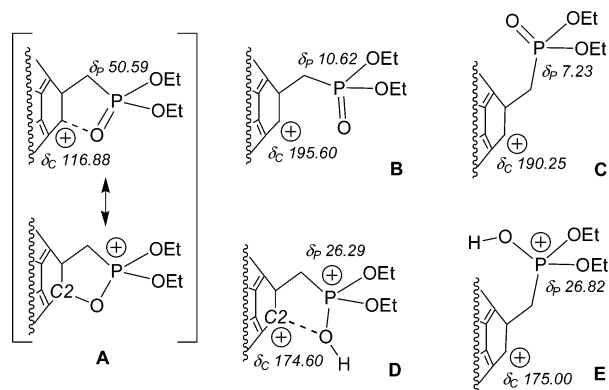


Figure 2. Possible structures of monocationic species (A–C) and their protonated dicationic structures (D and E), including the calculated NMR chemical shifts of C2 and P obtained by the GIAO method.¹²

minimized structure. This structure was calculated to be more stable than nonbridged structure E by 2.8 kcal mol⁻¹, the distance of C⁺...O in D being 3.252 Å. The results of GIAO calculations on D (174.60 ppm for C2 and 26.29 ppm for P)¹² were in agreement with the experimental values. Thus, we conclude that the most possible structure of the cationic species 1⁺ formed in H₂SO₄ is D with the cationic center coordinated by the protonated oxygen. For this structure, Mulliken charges on C2 and P are calculated as +0.084 and +0.658, respectively, while those of other 58 sp² carbons of the C₆₀ cage are in the range between +0.058 and -0.003, the sum of which amounts to +0.858.¹²

The rate of the formation of cation 1⁺ from 2 was found to depend not on the acidity but on the oxidizing ability of the acid used as a solvent; 1⁺ was generated immediately after dissolution in H₂SO₄ and FSO₃H (acidity function H₀, -12 and -15.1, respectively),¹⁴ whereas the generation of 1⁺ required more than 10 h in CF₃SO₃H (H₀, -14.1).^{14,15} Therefore, the direct protonolytic cleavage of the RC₆₀-H bond can be ruled out. When dimer 3 was used as the starting material instead of 2, cation 1⁺ was generated immediately in H₂SO₄, FSO₃H, and CF₃SO₃H¹⁵ as well. As the reaction mechanism, we assume that first the one-electron oxidation of 2 takes place to give radical cation 2^{•+}. Then, 2^{•+} would release the proton directly attached to the C₆₀ cage to give radical 1[•], which should be in equilibrium with dimer 3.⁸ The second one-electron oxidation of 1[•] can give cation 1⁺, similarly to the formation of azafullerenyl cation C₅₉N⁺ from its dimer.¹⁶

To confirm the above mechanism, one-electron oxidation of 2 and 3 was conducted in CH₂Cl₂ using a triarylammonium salt. When dimer 3 and two molar amounts of (2,4-Br₂C₆H₃)₃N⁺SbF₆⁻ (HSbF₆)_{0.5} (8),¹⁷ were mixed at room temperature for 15 min in CH₂Cl₂ under vacuum, a dark red solution with absorption maxima at 468 and 779 nm, with a weak and broad absorption in a NIR region, was obtained. Quenching this solution with TFE, allyltrimethylsilane, or benzene afforded the corresponding electrophilic addition product, 4, 6, or 7, in 72, 60, or 63% yield, respectively, indicating that cation 1⁺ was actually generated in CH₂Cl₂. When 2 was used as a starting material, which was less reactive than dimer 3 in oxidation in CF₃SO₃H, the treatment with three molar amounts of aminium salt 8 in CH₂Cl₂ also afforded a dark red solution. After 25 min, quenching this solution with allyltrimethylsilane gave 6 (45%) and dimer 3 (44%), while 11% of 2 remained unchanged, as judged from the ¹H NMR of the crude product. The formation of 6 indicates that cation 1⁺ was also generated from 2 through

one-electron oxidation with the aminium salt. The formation of dimer 3 confirmed the proposed mechanism.

In summary, a novel fullereryl cation 1⁺ was generated in sulfuric and sulfonic acids as well as in CH₂Cl₂ from monofunctionalized hydrofullerene 2 and from singly bonded fullerene dimer 3 through one-electron oxidation as a key step. Various nucleophiles, including nonactivated benzene,¹⁸ readily add to 1⁺ selectively at 2- or 4-positions, thus showing the possibility of these reactions to be used as a new way to functionalize fullerenes.

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Supporting Information Available: Experimental procedures, spectroscopic data, results of calculations (PDF), and X-ray crystallographic data for 8 (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) For reviews, see: (a) Reed, C. A.; Bolskar, R. D. *Chem. Rev.* **2000**, *100*, 1075. (b) Kitagawa, T.; Takeuchi, K. *Bull. Chem. Soc. Jpn.* **2001**, *74*, 785.
- (2) For an example of pentaaryl derivative, Ar₅C₆₀⁺, see: Avent, A. G.; Birkett, P. R.; Kroto, H. W.; Taylor, R.; Walton, R. M. *Chem. Commun.* **1998**, 2153.
- (3) Kitagawa, T.; Sakamoto, H.; Takeuchi, K. *J. Am. Chem. Soc.* **1999**, *121*, 4298.
- (4) Reed, C. A.; Kim, K.-C.; Bolskar, R. D.; Mueller, L. J. *Science* **2000**, *289*, 101.
- (5) There have been only a limited number of examples: (a) Yoshida, M.; Morinaga, Y.; Iyoda, M.; Kikuchi, K.; Ikemoto, I.; Achiba, Y. *Tetrahedron Lett.* **1993**, *34*, 7629. (b) Irgangring, H.; Weber, A. *Tetrahedron Lett.* **1997**, *38*, 2075. (c) Ohno, M.; Yashiro, A.; Tsunenishi, Y.; Eguchi, S. *Chem. Commun.* **1999**, 827. (d) ref 3.
- (6) (a) Hirsch, A. *The Chemistry of Fullerenes*; Thieme: Stuttgart, 1994. (b) Diederich, F.; Thilgen, C. *Science* **1996**, *271*, 317. (c) Taylor, R. *The Chemistry of Fullerenes*; World Scientific Publishing Co.: River Edge, NJ, 1996.
- (7) Allard, E.; Cheng, F.; Chopin, S.; Delaunay, J.; Rondeau, D.; Cousseau, J. *New J. Chem.* **2003**, *27*, 188.
- (8) Cheng, F.; Murata, Y.; Komatsu, K. *Org. Lett.* **2002**, *4*, 2541.
- (9) (a) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1991**, *113*, 4776. (b) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 523. (c) Wong, M. W.; Frisch, M. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 1645.
- (10) Structures were fully optimized at the B3LYP/6-31G* level in a gas phase, and then the molecular volumes were computed. By the use of the volume and the dielectric constant (ε = 101 for H₂SO₄), the structures were fully optimized at the same level of theory using the Onsager model.
- (11) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.
- (12) Based on the fully optimized structures at the B3LYP/6-31G* level of theory in a gas phase, the GIAO calculations were conducted using the B3LYP method and the basis sets 6-311G** for C, H, and O and 6-311+G(3df) for P.
- (13) Dillon, K. B.; Nisbet, M. P.; Waddington, T. C. *J. Chem. Soc., Dalton Trans.* **1981**, 212.
- (14) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; John Wiley & Sons: New York, 1985.
- (15) Although CF₃SO₃H is known as a nonoxidizing acid, (CF₃SO₂)₂O, which is inevitably formed during the distillation of CF₃SO₃H, can act as an oxidizing agent: Maas, G.; Stang, P. J. *J. Org. Chem.* **1981**, *46*, 1606.
- (16) Kim, K.-C.; Hauke, F.; Hirsch, A.; Boyd, P. D. W.; Carter, E.; Armstrong, R. S.; Lay, P. A.; Reed, C. A. *J. Am. Chem. Soc.* **2003**, *125*, 4024.
- (17) Compound 8 was newly synthesized and the structure determined by X-ray crystallography. Crystal data of 8: C₁₈H_{9.5}Br₆F₉Sb_{1.5}, M = 1072.85, rhombohedral, space group R-3c, a = 13.533(5) Å, c = 51.977(5) Å, V = 8244(4) Å³, Z = 12, F(000) = 5904, D_c = 2.593 g cm⁻³, μ(Mo Kα) 10.281 mm⁻¹, 109 variables refined on F² with 1618 observed reflections collected at 100 K (θ_{max} = 25.0°) with I ≥ 2σ(I) yielding R₁ = 0.0675, wR₂ = 0.1690. For the same radical cation having other counteranions, see: (a) Schmidt, W.; Steckhan, E. *Chem. Ber.* **1980**, *113*, 577. (b) Bolskar, R. D.; Mathur, R. S.; Reed, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 13093.
- (18) Anisole is reported to react with monofunctionalized C₆₀ cations: Kitagawa, T.; Lee, Y.; Hanamura, M.; Sakamoto, H.; Konno, H.; Takeuchi, K.; Komatsu, K. *Chem. Commun.* **2002**, 3062.

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