Formation and Characterization of Polysultonated C_{60}

Glen P. Miller,* Mihai A. Buretea, Marcelino M. Bernardo, Chiang S. Hsu and Howard L. Fang

Corporate Research Laboratories, Exxon Research & Engineering Co., Annandale, NJ 08801, USA

C_{60} reacts with SO_3, either neat or in fuming sulfuric acid (FSA), to form a polysultone, $C_{60}(SO_3)_x$; reaction in FSA yields a polysultone with average structure $C_{60}(SO_3)_{5.2}$.

The chemistry of fullerenes continues to be of great interest.[1] Previously, we reported the facile oxidation of fullerenes in superacidic media.[2,3] Paramagnetic and diamagnetic cations of indefinite stability are generated in Magic Acid[2] while a species giving rise to a ground-state triplet EPR signal, presumably $[C_{60}]^{2+\cdot 2}$; is initially formed in fuming sulfuric acid (FSA).[3] We now report the reactivity of C_{60} with sulfur trioxide, either neat SO_3 or in FSA, to form the corresponding polysultones of C_{60}, $C_{60}(SO_3)_x$.

Contacting C_{60} with FSA results in the immediate formation of a green, EPR active solution with absorption maxima in its UV–VIS–NIR spectrum at 824 and 959 nm, characteristic of fullerene radical cation formation.[2,3] Unlike the case in Magic Acid,[2] fullerene radical cations show limited kinetic stability in FSA. Thus, the line shape of their EPR spectra varies as a function of time spent at room temperature (Fig. 1) indicating in situ reactivity of the radical cation. The total EPR spin count of the sample decreases rapidly at room temperature. Concurrently, the colour of the mixture changes from green to orange. After approximately 24 h at room temperature, an orange–red, EPR silent solid, **1**, precipitates from solution. Likewise, room temperature UV–VIS–NIR spectra reveal disappearance of the radical cation bands at 824 and 959 nm simultaneous to the growth of new absorption bands of **1** in the visible. The data suggest that fullerene radical cations are intermediates along the reaction path leading to **1**.

FTIR spectra of **1** (Fig. 2) reveal strong SO_2 stretching vibrations centred at 1425 (asymmetric) and 1225 (symmetric) cm^{-1} as well as strong C–O stretching vibrations at 950, 978 and 1001 cm^{-1}; and no X–H stretching vibrations of any kind where X may be C, O, S, etc. The high frequency SO_2 stretching vibrations are characteristic of a select few structures: organic sulfonyl halide, sulfonic acid, organic sulfonate and organic sulfate. Sulfonyl halide formation is an impossibility since halogen free reactants were utilized. Likewise, the absence of O–H stretching bands in Fig. 2 eliminates sulfonic acid formation from consideration. While either sulfonate (*i.e.* sultone) or sulfate (*i.e.* cyclosulfate) formation seems plausible in FSA (Scheme 1), further investigation demonstrated that dry SO_3 (liquid or gaseous) reacts directly with C_{60} affording a product with FTIR spectrum identical to that of **1**. Thus, **1** must be a polysultone of C_{60}.

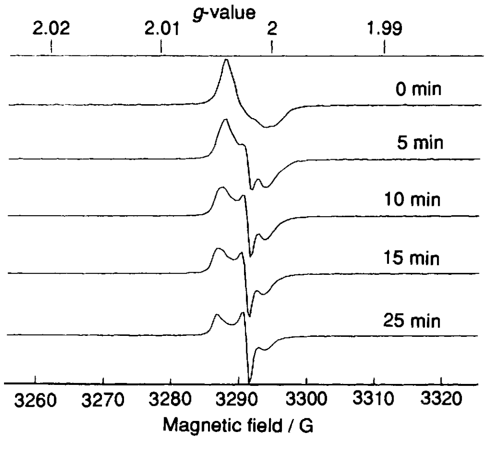


Fig. 1 Normalized EPR spectra of a freshly prepared C_{60}/FSA mixture as a function of time spent at room temperature. Spectra were recorded at 80 K on a Varian E-line Century Series EPR Spectrometer. Conditions: microwave frequency: 9.2217 GHz; microwave power: 1 μW; modulation amplitude: 1 G; scan time: 2 min.; sweep width: 80 G.

Interestingly, interaction of C_{60} with dry SO_3, liquid or gaseous, does not lead to a long-lived green complex as in FSA. Collapse of the $[C_{60}]^{\cdot +}$ $[SO_3]^{\cdot -}$ radical-ion pair into sultone product (Scheme 1) may occur immediately upon its formation in the absence of a cation sustaining solvent of low

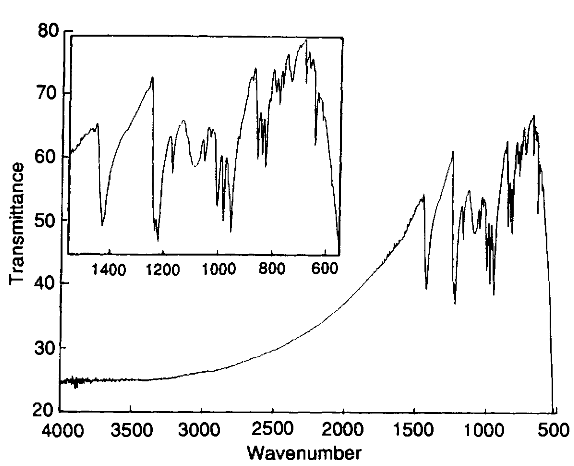
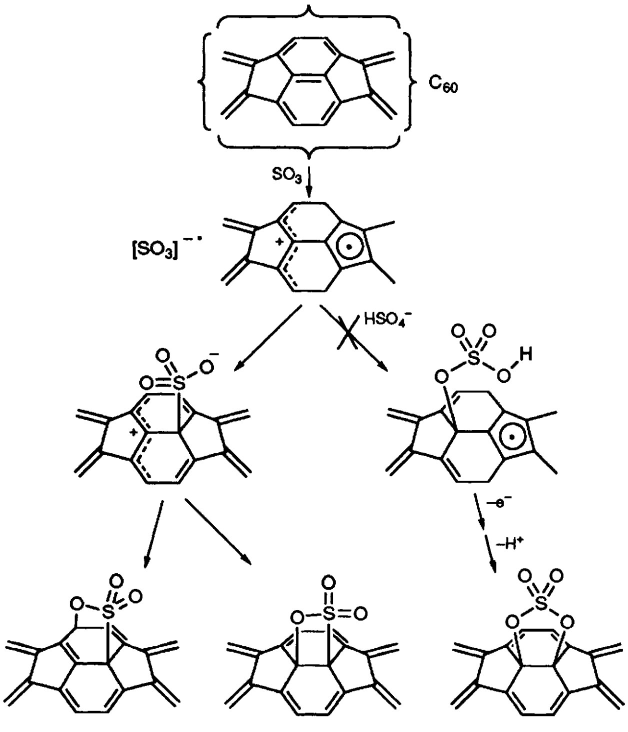


Fig. 2 FTIR spectrum of **1** on a polished NaCl disc prepared by suspending $CHCl_3$ solution of **1** on disc and evaporating solvent under N_2. 32 scan spectrum with 1 cm^{-1} resolution recorded on a Nicolet Magna-IR 550 spectrometer.



Scheme 1 Sultone *vs.* cyclosulfate formation

nucleophilicity. Alternatively, reaction with anhydrous SO_3 may proceed via a concerted cycloaddition as has been suggested for other alkenes.[4,5,6] Whether formed in a stepwise or concerted manner, the sultone functionality may bridge the C_{60} skeleton in either a 1,4- (*i.e.* δ-sultone) or a 1,2- fashion (β-sultone). δ-Sultones are generally more stable than β-sultones as evidenced by the often facile and irreversible rearrangement of the latter into the former.[6] However, β-sultones bearing electronegative halogen functionalities in the ring have been isolated as stable molecules.[6] It remains to be seen whether the electronegative fullerene skeleton stabilizes β-sultone formation.

Further evidence of C–S bond formation in **1** comes from FT-Raman experiments. In addition to broad absorptions of medium intensity at 1432 and 1223 cm^{-1}, C–S absorptions of medium intensity are observed at 700–725 cm^{-1}. Moreover, solution phase ^{13}C NMR spectra of **1** in either d_6-DMSO or d_7-DMF reveal two broad, overlapping ^{13}C signals at 72 (*C*–S) and 78 (*C*–O)† ppm as well as one large, fullerenic signal centred at 147 ppm (C=C). With chromium(III) acetylacetonate added as relaxation agent, the same set of three signals are observed, but the high field signals have shifted to 78 and 81 ppm presumably due to interaction of the metal with the sultone functionality.

Several soft ionization methods have been utilized for the mass spectrometry study of **1**, but no molecular ions have been observed. Degradation of **1** accompanies desorption–vaporization under all conditions studied. Degradation products under thermal desorption negative-ion chemical ionization (TDNICI) conditions appear as fullerene oxides in the TDNICI mass spectra. Prominent signals at *m/z* equal to 816 ($C_{60}O_6$), 800 ($C_{60}O_5$), 784 ($C_{60}O_4$), 768 ($C_{60}O_3$), 752 ($C_{60}O_2$), 736 ($C_{60}O$), and 720 (C_{60}) are observed and correspond to fragmentation products following extrusion of SO_2.

Thermal gravimetric analysis of **1** with FTIR detection of evolved gases (TGA-FTIR) confirms thermal extrusion of SO_2 under fairly mild conditions (Fig. 3). Water evolves first from the hygroscopic **1** and accounts for as much as 12% of the total weight when fully hydrated. At approximately 130 °C, SO_2 evolution from **1** begins as evidenced by weight loss in the thermogram (Fig. 3) and simultaneous FTIR detection of gaseous SO_2. No other S-bearing gas is detected during thermolysis. The first derivative of the TGA curve reveals a maximum rate of SO_2 evolution at approximately 200 °C and the completion of SO_2 evolution by 275 °C. X-ray photoelectron spectroscopic (XPS) analysis of **1** before and after thermolysis indicates complete removal of S as SO_2.

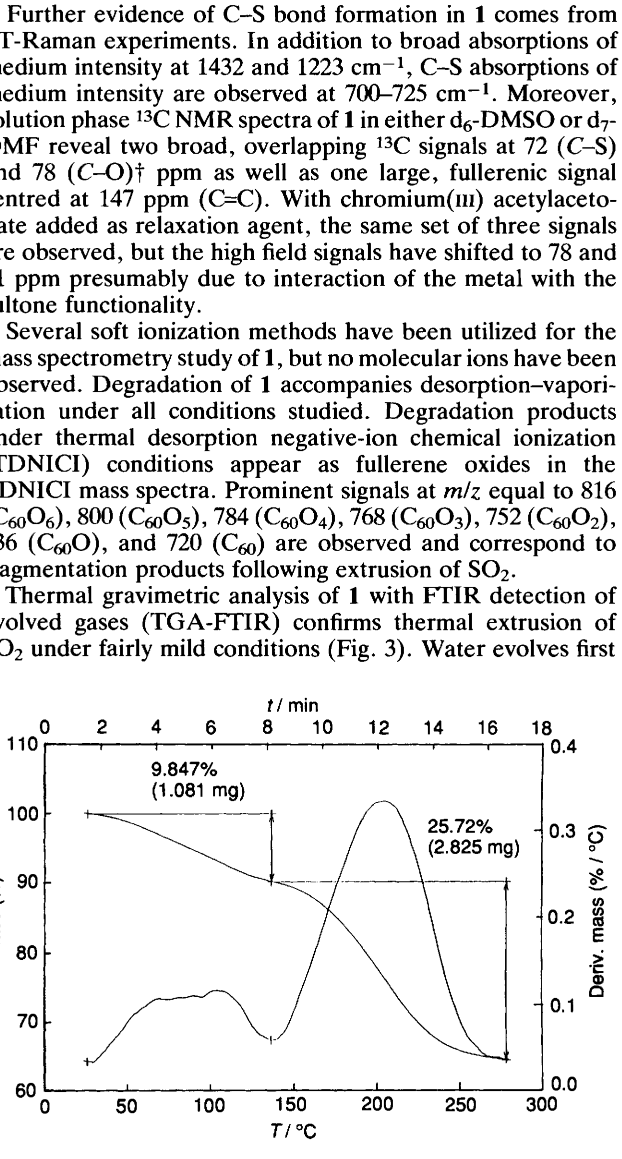


Fig. 3 TGA thermogram and first derivative curve of **1**. Thermogram recorded on a TA Instruments TGA 51 Thermogravimetric Analyzer under a stream of dry N_2. Gases evolved during heating are piped to and continuously detected by Nicolet Magna-IR 550 spectrometer.

Disregarding water of hydration, TGA results indicate 29% average weight loss from **1** during SO_2 extrusion, consistent with an average starting structure of $C_{60}(SO_3)_{5.1}$. Elemental analysis on fully hydrated **1** suggests a similar structure, $C_{60}(SO_3)_{5.3}$.‡ Reactions with stoichiometric SO_3 are now underway in an attempt to form the mono-functionalized C_{60} sultone. We are also investigating the structure of the interesting thermolysis products (after SO_2 extrusion) of C_{60} polysultones.

The authors thank Steven R. Lindstrom for technical assistance and the Exxon Corporate Research Summer Intern Program for partial support of MAB in 1993.

Received, 1st March 1994; Com. 4/01255K

Footnotes

† SpecCal, the Spectrum Estimation Feature of the STN International ^{13}C NMR Database, estimates for C–O, C–S ^{13}C NMR chemical shift pairs for β-sultones: 1,1,2,2-tetrahydro-1,2-ethylene sultone, $C_2H_4(SO_3)$: 62.15 ± 6.78, 60.87 ± 10.10; 1,1,2,2-tetraphenyl-1,2-ethylene sultone: 77.14 ± 3.54, 75.29 ± 2.08; 1,1,2,2-tetrafluoro-1,2-ethylene sultone, $C_2F_4(SO_3)$: 107.76 ± 6.83, 80.21 ± 6.77. Akiyama *et al.* (*Bull. Chem. Soc. Japan*, 1978, *51*, 1251) report ^{13}C shifts of 71.5 and 50.1 ppm for the C–O and C–S carbons of isoprene-1,4-sultone, a β-γ unsaturated δ-sultone.

‡ Elemental analysis on fully hydrated **1** performed by Quantitative Technologies Incorporated, Whitehouse, New Jersey. Found: 55.37% C, 13.02% S, 1.29% H; TGA: 12.0% H_2O. Calculated for $C_{60}(SO_3)_{5.30}\cdot(H_2O)_{8.69}$: 55.37% C, 13.06% S, 1.34% H, 12.03% H_2O.

References

1 See, for example: R. Taylor and D. R. M. Walton, *Nature*, 1993, **363**, 685; G. P. Miller, *Chemistry & Industry*, 1993, **7**, 226; G. A. Olah, I. Bucsi, R. Aniszfeld and G. K. S. Prakash, *Carbon*, 1992, **30**, 1203.
2 G. P. Miller, C. S. Hsu, H. Thomann, L. Chiang and M. Bernardo, *Mat. Res. Symp. Proc.* 1992, **247**, 293.
3 H. Thomann, M. Bernardo and G. P. Miller, *J. Am. Chem. Soc.*, 1992, **114**, 6593.
4 M. Nagayama, O. Okumura, S. Noda, H. Mandai and A. Mori, *Bull. Chem. Soc. Japan*, 1974, **47**, 2158.
5 D. W. Roberts, D. L. Williams and D. Bethell, *J. Chem. Soc., Perkin Trans. 2*, 1985, 389.
6 D. W. Roberts and D. L. Williams, *Tetrahedron* 1987, **43**, 1027.