Pergamon

Tetrahedron Letters, Vol. 37, No. 41, pp. 7409-7412, 1996

0040-4039/96 $15.00 + 0.00

PII: S0040-4039(96)01613-9

A New Method for Facile and Selective Generation of C_{60}^- and C_{60}^{2-} in Aqueous Caustic/THF(or DMSO)

Mingfei Wu, Xianwen Wei, Ling Qi and Zheng Xu*

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry,
Nanjing University, Nanjing 210093, P.R.China

Abstract: Selective reduction C_{60} to C_{60}^- and C_{60}^{2-} has been accomplished by treating C_{60} with zinc powder (or sodium hydrosulfite) in aqueous caustic/THF(or DMSO). It was confirmed that C_{60}^- and C_{60}^{2-} did not react with water at our experimental conditions.

Since the discovery of superconductivity for K_3C_{60}, the C_{60}^{n-} anion has attracted considerable interest. The C_{60}^{n-}(n=1- 6) have now been synthesized by electrochemical or chemical methods.[1,2] Very recently, there has been a few reports[3] describing several methods for the non-aqueous solution-phase generation of C_{60}^{n-}(n=1,2,3) . Most of them require the stoichiometric control of the reducing agents. It is an inconvenient operation because the reducing agents are usually very sensitive to air and moisture, which limits the potential utility of these methods.

We report here a facile and selective method for the aqueous solution phase generation of C_{60}^- and C_{60}^{2-} by treating C_{60} with zinc powder (or sodium hydrosulfite) in aqueous caustic/THF(or DMSO). We found that C_{60}^- and C_{60}^{2-} are very sensitive to oxygen, but inert to water. Actually, they are stable in water (exclude oxygen!) for at least several months. All solvents used in our experiments are oxygen-free. THF was distilled under argon. Argon was bubbled through water and DMSO under reflux for 10 min.

In a typical experiment 34.0 mg C_{60} powder(0. 047 mmol) , 130 mg zinc powder (2 mmol, excess) and 400 mg solid NaOH pellets(10 mmol) was put in a bottle, air was pumped out from bottle to exclude oxygen, filled with argon and then 20 ml THF was added to it with stirring. All the reaction starting materials did not dissolve in the THF. After adding 5 ml of water (exclude oxygen!) , NaOH solid pellets dissolved in the water, but C_{60} and zinc powder were suspended in the interface between THF(upper layer) and aqueous caustic(lower layer) . The reduction took place rapidly and the red cloud-like reaction product diffused into the THF layer in which the color turned to dark red-purple very quickly. After 10 min the dark red-purple THF solution was separated from the colorless aqueous caustic and used directly for electrospray mass spectroscopy (ESI-MS). Fig.1a is an ESI- MS and there is only a very strong peak at m/e=720 with anion mode, the very minor peak at m/e=736 is $C_{60}O$ generated from reaction of C_{60}^- and trace oxygen in THF. Because C_{60} does not dissolve totally in THF, the peak at m/e=720 belongs to C_{60}^- unambiguously. The VIS-NIR spectrum of the dark red-purple solution has absorption bands at 1075 and 994nm (Fig.1d), and these can be unambiguously assigned to C_{60}^- .[1f,3c,4] The ^{13}C-NMR(298K) of this solution in which D_2O(exclude oxygen!) was added has a single peak with line width 3ppm at 188.2ppm and the ESR spectrum had a sharp peak(T=110K) with ΔH=2G at g=1.9998. These are also characteristics[1f,3b,3c,5] of C_{60}^-. Radiofrequency Inductively Coupled Plasma(ICP) analysis data shown that the counterpart cation is Na^+, forming an NaC_{60} compound in THF solution.

Using $Na_2S_2O_4$ as a reducing agent for generation of C_{60}^- in aqueous caustic/THF, we attained the same results as for zinc powder . The ESI-MS, and VIS-NIR spectrum are shown in Fig.2.

Although the zinc powder (or sodium hydrosulfite) used in our experiments is in excess, only the monoanion C_{60}^- is generated in aqueous caustic/THF. Zinc powder and sodium hydrosulfite are commonly available , cheap and stable in air, also we do not require stoichiometric control.This the new methode is very convenient.

Using DMSO as a solvent instead of THF, we attained a dark red-brown solution under similar experimental conditions for the monoanion C_{60}^- generation. The VIS-NIR absorption spectrum of the dark red-brown solution shows that there the 1075 and 994 nm bands are absent and new bands appear at 945 and 836 nm (Fig.1e) which are characteristic[1f,3c,4] of dianion C_{60}^{2-}. It indicated that there was no monoanion C_{60}^- in the solution. The ESR spectrum of the frozen(T=110K) dark red-brown solution is also characteristic[5] of dianion C_{60}^{2-} and consists of a sharp peak (g=2.0000, ΔH=3G) superimposed on a pair with a separation of 9.2G.

The selective chemical generation of C_{60}^- or C_{60}^{2-} in THF or DMSO can be rationalized by considering the relevant redox potentials for C_{60}^-/C_{60}^{2-} in solvents with varying polarity (Table.1).

Table.1 $E_{1/2}$ of various C_{60} anions in several solvents in 0.1 M $(TBA)ClO_4$
$E_{1/2}$ (V) (vs. SCE)

Solvent	C_{60}^0/C_{60}^-	C_{60}^-/C_{60}^{2-}	C_{60}^{2-}/C_{60}^{3-}	C_{60}^{3-}/C_{60}^{4-}	reference
THF	-0.33	-0.92	-1.49	-1.99	6
THF	-0.35	-0.93	-1.43	-2.01	this work
DMF	-0.26	-0.72	-1.31	-1.85	6
DMSO	-0.16	-0.66	------	------	this work

The $E_{1/2}$ of $C_{60}^{0/-}$ and $C_{60}^{-/2-}$ couples in DMSO are located at -0.16V and -0. 66V (vs. SCE) which shifts to more positive than in THF, so the reduction potentials of zinc powder and sodium hydrosulfite become sufficiently negative to reduce C_{60} to C_{60}^{2-}.

The cyclovoltammogram of C_{60}^- in THF (because C_{60} does not dissolve totally in THF, it is better to use C_{60}^- instead of C_{60} as a starting material) shows that $E_{1/2}$ of C_{60}^0/C_{60}^-, C_{60}^-/C_{60}^{2-} and

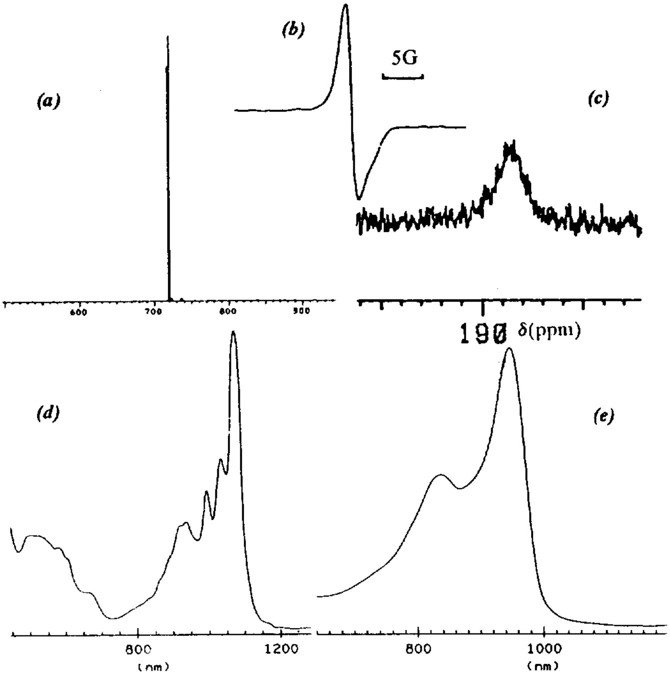

Fig. 1 C_{60} anions generated by reaction of C_{60} and zinc powder in aqueous caustic/THF(or DMSO) .
(*a*) ESI-MS; (*b*) ESR; (*c*) ^{13}C-NMR; (*d*) NIR spectra of C_{60}^{-} in THF.
(*e*) NIR spectrum of C_{60}^{2-} in DMSO.

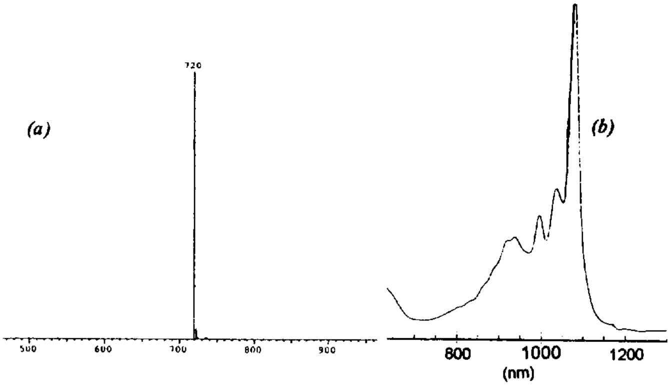

Fig. 2 (*a*) ESI-MS; (*b*) NIR spectra of C_{60}^{-} generated by reaction of C_{60} and $Na_2S_2O_4$ in aqueous caustic/THF.

C_{60}^{2-}/C_{60}^{3-} couples are located at -0.87V ,-1.48V and -2.03V (vs. Fc) separately. After addition of some water(exclude oxygen!), there is a large peak(~ -1.9V vs. Fc) between C_{60}^{-}/C_{60}^{2-} and C_{60}^{2-} /C_{60}^{3-} which corresponds to redox of water. In the cyclovoltammogram of C_{60}^{2-} in DMSO, the $E_{1/2}$ of C_{60}^{0}/C_{60}^{-} and C_{60}^{-}/C_{60}^{2-} are located at -0.11V and -0.61V (vs. Ag-AgCl) separately and also the peak of redox of water appears between C_{60}^{-}/C_{60}^{2-} and C_{60}^{2-}/C_{60}^{3-} (at ~ -1.0V). This confirmed that C_{60}^{-} and C_{60}^{2-} cannot reduce the water.

In conclusion, C_{60} mono- and dianions can be generated by reaction of C_{60} with zinc powder or sodium hydrosulfite in aqueous caustic/THF(or DMSO), without stoichiometric control. To our knowledge, it is the first confirmation that C_{60}^{-} and C_{60}^{2-} do not react with water under our experimental conditions. Efforts are now under way to use this method to synthesize and characterize various new fulleride salts and organo-fullerenes with a variety of electophiles.

We thank National Natural Science Foundation of China and State Education Commission Doctoral Foundation of China for financial support of this work. We are also indebted to Mr. K. Y. Zhou and Y. C. Cao for help to determine the ESI-MS.

REFERENCES:

1. (a) Dubois, D.; Kadish, K.M.; Flanagan, S.; Haufler, R.E.; Chibante, L.P.F. and Wilson, L.J. *J.Am.Chem.Soc.*, **1991**, 113, 4364; (b) Dubois, D.; Kadish, K.M.; Flanagan, S. and Wilson, L.J. *J.Am.Chem.Soc.*, **1991**, 113, 7773; (c) Xie, Q.; perez-cordero, E.; Echegoyen, L.J. *J.Am.Chem.Soc.*, **1992**, 114, 3978; (d) Ohsawa, Y. and Saji, T. *J.Chem.Soc., Chem.Commun.*, **1992**, 781; (e) Zhou, F.; Jehoulet, C. and Bard, A.J. *J.Am.Chem.Soc.*, **1992**, 114, 11004; (f) Khaled, M.M.; Carlin, R.T.; Trulove, P.C.; Eaton, G.R. and Eaton, S.S. *J.Am.Chem.Soc.*, **1994**, 116, 3465.
2. (a) Bossard, C.; Rigaut, S.; Astruc, D.; Delville, M.H.; Felix, G.; Févrir-Bouvier, A.; Amiell, J.; Flandrois, S. and Delhaes, P. *J.Chem.Soc., Chem.Commun.*, **1993**, 333; (b) Bhyappa, P.; Paul, P.; Stinchcombe, J.; Boyd, P.D.W. and Reed, C.A. *J.Am.Chem.Soc.*, **1993**, 115, 11004; (c) Bausch, J.W.; Prakash, G.K.S.; Olah, G.A.; Tse, D.S.; Lorents, D.C.; Bae, Y.K. and Malhotra, R. *J.Am.Chem.Soc.*, **1991**, 113, 3205.
3. (a) Liu, X.H.; Wan, W.C.; Owens, S.M. and Broderick, W.E. *J.Am.Chem.Soc.*, **1994**, 116, 5489; (b) Douthwaite, R.E.; Brough, A.R. and Green, M.L.H. *J.Chem.Soc., Chem.Commun.*, **1994**, 267; (c) Subramanian, R.; Boulas, P.; Vijayashree, M.N.; Souze, F.D.; Jones, M.T. and Kadish, K.M. *J.Chem.Soc., Chem.Commun.*, **1994**, 1847; (d) Chen, J.; Huang, Z.E.; Cai, R.F.; Shao, Q.F.; Chen, S.M. and Ye, H.J. *J.Chem.Soc.,Chem.Commun.*, **1994**, 2177; (e) Zhang, W.; Wu, Z.Z.; Zhu, H.; Tao, W.C.; Qi, L.; Xu, Z. and You, X.Z. *Chin.Chem.Lett.*, **1994**, 5(2), 145.
4. Lawson, D.R.; Feldheim, D.L.; Foss, C.A.; Dorhout, P.K.; Elliott, C.M.; Martin, C.R. and Parkinson, B. *J.Electrochem.Soc.*, **1992**, 139, L68.
5. Dubois, D.; Jones, M.T.; Kadish, K.M. *J.Am.Chem.Soc.*, **1992**, 114, 6446.
6. Dubois, D.; Moninot, G.; Kvtner, W.; Jones, M.T. and Kadish, K.M. *J.Phys.Chem.*, **1992**, 96, 7137.

(*Received in China* 4 *October* 1995; *revised* 27 *December* 1995; *accepted* 21 *May* 1996)