J. Am. Chem. Soc. **1996,** *118,* 4693−4698

Disproportionation of Photoexcited C_{60}

Che Chau Yang and Kuo Chu Hwang*

Contribution from the Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, Republic of China

Received August 7, 1995[⊗]

Abstract: Irradiation of C_{60}-toluene solution at room temperature affords two ESR bands with g and ΔH_{pp} values of (2.0013, 0.5 G) and (2.0024, 0.75 G), respectively. In the presence of 6% methanol or 12% benzonitrile, the latter band disappears completely. Below 200 K, only the former band was observed. They were assigned to be $^3C_{60}$ and $C_{60}^{\bullet+}$, respectively. In the presence of tetraphenylphosphonium tetraphenylborate, the g value of the $C_{60}^{\bullet+}$ cation radical shifts to 2.0006, and an additional broad band of $g = 1.9992$ and $\Delta H_{pp}= 30$ G was observed. Upon cooling, the line width of this new band drops from 30 G at 300 K to 4 G at 77 K. This new band was assigned to be the $C_{60}^{\bullet-}$ anion radical according to its characteristic behavior. At room temperature, photolysis causes the C_{60}−toluene solution's color to turn from purple to brown, and then brown precipitates formed. Desorption chemical ionization (DCI) mass analysis of the brown precipitates indicates the formation of $C_{60}{\bullet}H_n(\text{tolyl})_n$ ($n = 1-4$) adducts. The formation of $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ was rationalized in terms of disproportionation of two $^3C_{60}$. The brown precipitates were due to the chemical reaction between the $C_{60}^{\bullet+}$ cation radical and the solvent molecules, which rationalizes the "photodegradation" of fullerene as reported in literature. The important role of the $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ to the peculiar photochemical behavior of fullerene solutions or films, such as nonlinear optical property, photoinduced polymerization in solid film, nonlinear photoconductivity, etc, will be discussed.

Introduction

Large scale production of fullerenes[1] has initiated a number deal of studies in this new form of carbon allotrope. Cyclic voltametric studies show that the first reduction potential and the first oxidation potential of C_{60} are −0.43 in methylene chloride[2a] and +1.76 V_{SCE} (vs saturated calomel electrode) in benzonitrile,[2b] respectively. The relatively low reduction potential implies that C_{60} is a good electron acceptor. Photochemical studies have revealed that all singlet, triplet, and ground state C_{60}s are good electron acceptors.[3] Recently, some experiments also suggest that C_{60} can serve as electron donor.[4] Upon photoexcitation, singlet C_{60} undergoes intersystem crossing to generate triplet excited state with quantum yield of nearly unity.[5] The triplet C_{60} can be observed by ESR measurements.[6] Closs and co-workers[6b] observed an ESR band of $g = 2.00135$ and $\Delta H_{pp} = 0.14$ G from a C_{60}−methylcyclohexane solution upon UV irradiation. They studied the intensity decay profile and assigned it to be $^3C_{60}$. Levanon et al.[6c] observed an ESR band from a C_{60}−toluene solution at 300 ns delay after laser excitation and assigned it to be $^3C_{60}$. At a later ($t > 1$ μs) time scale, they detected another rising band with $g = 2.0016$ and proposed it to be the unpaired, delocalized electron in C_{60} aggregates. Steren et al.[6d] irradiated a C_{60}−benzonitrile solution at 300 K and observed an ESR band with $g = 2.0012$ and $\Delta H_{pp} = 0.3$ G. The ESR band has the same lifetime as that of triplet C_{60} as measured by flash photolysis. Zhang and co-workers[6e] measured the T_1 and ^{13}C hyperfine coupling constant of $^3C_{60}$ in methylcyclohexane at 300 K.

C_{60} was also reported to be light sensitive.[7] In the presence of oxygen, energy transfer from triplet C_{60} generates singlet oxygen which further reacts with the C=C double bonds of the fullerene cage to generate $C_{60}O$ and other unidentified products.[8] In the absence of oxygen, however, irradiation of C_{60} solution also causes slow transformation of C_{60} to brown precipitates.[9] The brown precipitates were never identified, not to mention the degradation mechanism. In this paper, we report that excited state C_{60} molecules undergo disproportionation to generate cation and anion radicals. Subsequent reaction of the C_{60} radical cation with solvent molecules leads to the formation of brown precipitates and color changes of the solution.

Results and Discussion

At 230 K, irradiation of a C_{60} toluene solution affords two ESR bands; the right one with a g value of 2.0013 and a peak to peak width, ΔH_{pp}, of 0.5 G (hereafter band a), and the left one with $g = 2.0024$ and $\Delta H_{pp} = 0.75$ G (hereafter band b, see

---

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1996.

(1) Krätschmer, W; Lamb, L. D.; Föstiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(2) (a) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (b) Dubois, D.; Kadish, K. M.; Fanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 7773.

(3) (a) Sension, R. J.; Szarka, A. Z.; Smith, G. R.; Hochetrasser, R. M. *Chem. Phys. Lett.* **1991**, *185,* 179. (b) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277. (c) Hwang, K. C.; Mauzerall, D. *J. Am. Chem. Soc.* **1992**, *114*, 9705.

(4) (a) Nadtochenko, V. A.; Denisov, N. N.; Rubtsov, I. M.; Lobach, A. S.; Moravkii, A. P. *Chem. Phys. Lett.* **1993**, *208,* 431. (b) Michaeli, S.; Meiklyar, V.; Schulz, M.; Möbius, K.; Levanon, H. *J. Phys. Chem.* **1994**, *98,* 7444. (c) Lem, G.; Schuster, D. I.; Courtney, S. H.; Lu, Q.; Wilson, S. R. *J. Am. Chem. Soc.* **1995**, *117*, 554.

(5) Arbogast, J. W.; Darmanyan, A. P.; Foote, C. S.; Rubin, Y.; Diederich, F. N.; Alvarez, M. M.; Anz, S. I.; Whetten, R. L. *J. Phys. Chem.* **1991**, *95*, 11.

(6) (a) Wasielewski, M. R.; O'Nell, M. P.; Lykke, K. R.; Pellin, M. J.; Gruen, D. M. *J. Am. Chem. Soc.* **1991**, *113*, 2774 (b) Closs, G. L.; Gautam, P.; Zhang, D.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem.* **1992**, *96*, 5228. (c) Levanon, H.; Meiklyar, V.; Michaeli, A.; Michaeli, S.; Regev, A. *J. Phys. Chem.* **1992**, *96*, 6128. (d) Steren, C. A.; Willigen, H. van; Dinse, K. P. *J. Phys. Chem.* **1994**, *98*, 7464. (e) Zhang, D.; Norris, J. R.; Krusic, P. J.; Wasserman, E.; Chen, C. C.; Lieber, C. M. *J. Phys. Chem.* **1993**, *207*, 339.

(7) Taylor, R.; Parsons, J. P.; Avent, A. G.; Rannard, S. P.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *Nature* **1991**, *351*, 277.

(8) (a) Creegan, K. M.; Robbino, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M. *J. Am. Chem. Soc.* **1992**, *114*, 1103. (b) Heymann, D.; Chibante, L. P. F. *Chem. Phys. Lett.* **1993**, *207*, 339.

(9) Juha, L.; Krása, J.; Láska, L.; Hamplová, V.; Soukup, L.; Engst, P.; Kubát, P. *Appl. Phys. B.* **1993**, *57*, 83.

S0002-7863(95)02640-0 CCC: $12.00

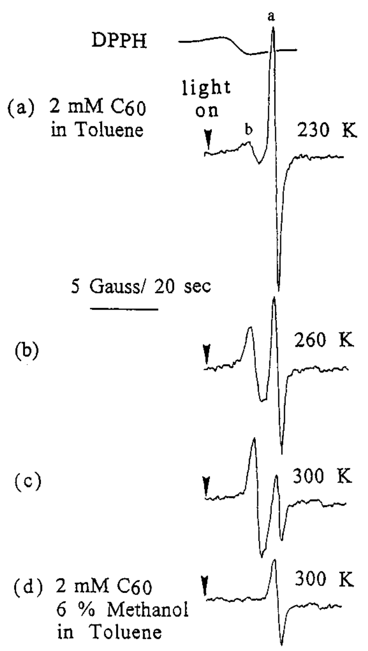

Figure 1. Steady state ESR spectra of 2.0 mM C_{60}−toluene solution irradiated by a 500 W high pressure mercury lamp at temperature of (a) 230 K, (b) 260 K, and (c) 300 K. The spectrum in (d) is under the same condition as in (c) except in the presence of additional 6% methanol in the solution. The microwave power is 18 dB and modulation 2 G_{pp} in all experiments.

Figure 1a). At higher temperatures, the intensity of band a decreases in association with the growth of band b (see Figure 1b,c).[10] Band b disappears completely in the presence of 6% methanol (see Figure 1d) or 12% of benzonitrile (data not shown). At a lower percentage of benzonitrile, the band b appears at first and gradually disappears at a latter time, while band a was not affected by the presence of either methanol or benzonitrile. Below 200 K, only band a can be observed. When the solvent was changed to benzene, only band a can be observed at all temperatures (180−330 K, data not shown). The intensity of band a is very sensitive to the presence of molecular oxygen. Insufficient deoxygenation causes complete disappearance of band a. The observed line width of band a remains the same within 200−300 K, i.e., 0.5 G. Upon light off, both bands a and b disappear immediately (within the time constant, 0.5 s, of the ESR spectrometer).

Figure 2 shows the ESR spectra taken from the C_{60}−$(ph)_4P^+(ph)_4B^-$−toluene system. Without light, no signal was observed. When a light is on, two ESR bands were observed: the previously detected band a as well as a small band (hereafter, band b′) with $g = 2.0006$ and ΔH_{pp} of 1.25 G (Figure 2 a−c). The previously observed band b (Figure 1) was not observed here. At longer irradiation time, band a diminishes, and the intensity of band b′ increases slowly. Meanwhile, another very broad signal (hereafter, band c) grows. If light was turned off, band a disappears immediately (within the time constant, 0.5 s, of the ESR spectrometer), whereas bands b′ and c remain unchanged, indicating the short-lived, nonionic feature of band a, and the long-lived, ionic character of bands b′ and c. In other words, bands b′ and c are due to ionic radical species and most probably stabilized by their counter ions of the organic salt. At very long irradiation time, bands b′ and c grow even more, and band a was covered by the very broad feature of band c. Band c has a *g* value of 1.9992 and ΔH_{pp} of 30 G at 300 K (Figure 2d−h). When 6% of methanol was added into the system (before irradiation, see Figure 2i), band b′ disappears, indicating the electron deficient (or cationic) character of band b′.

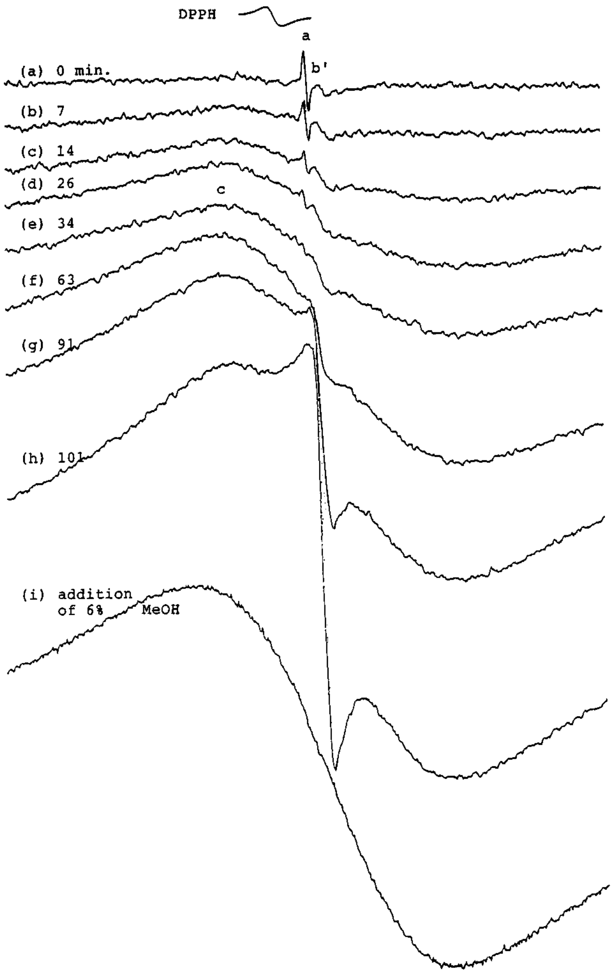

Figure 2. ESR spectra of a C_{60} (2 mM)−$(ph)_4P^+(ph)_4B^-$(4.5 mM)−toluene solution with various irradiation time: (a) 0, (b) 7, (c) 14, (d) 26, (e) 34, (f) 63, (g) 91, and (h) 101 min. The spectrum in (i) was obtained from a sample under the same condition except the presence of 6% methanol in the solution, of which the irradiation time is 2 h.

To assign identities, we compare the observed features of bands a, b, b′, and c with literature data. The reported *g* values for $^3C_{60}$ in literature are very similar, ranging from 2.0012 to 2.00135.[6] Laser flash photolysis study shows that molecular oxygen can efficiently quench $^3C_{60}$ and reduces the lifetime or the steady state concentration of $^3C_{60}$.[5] The band a has a g value of 2.0013 and is very sensitive to the presence of molecular oxygen. In addition, the *g* value of band a does not shift in the presence of organic salts, nor does band a disappear in the presence of nucleophiles (methanol and benzonitrile), which indicates the nonionic nature of the species responsible for band a. Based on the above features, we tentatively attribute band a to the $^3C_{60}$.[11] The assignment is consistent with other observations that the decrease in the intensity of band a is

---

(10) At longer irradiation time, the ratio of $C_{60}{}^{\bullet+}$ vs $^3C_{60}$ gradually increases. To compare the effect of temperature, the irradiation time was maintained to be the same for all samples.

(11) In ESR experiments, a larger modulation will lead to a higher magnitude of ESR intensity. The observed line width will, however, be distorted (or increased) if the modulation is larger than the true line width (see: Poole, C. P. Jr. *Electron Spin Resonance*, 2nd ed.; John Wiley & Sons: New York, 1983; pp 229−247). We chose a modulation of 2 G to enhance the otherwise too-small triplet C_{60} band. Therefore, our observed line width, 0.5 G, for the $^3C_{60}$ band is larger than the 0.14 G value reported by Closs and co-workers (ref 6b). Similarly, our observed line width for the $C_{60}{}^{\bullet+}$ band is larger than its true value. The observed value for the $C_{60}{}^{\bullet-}$ band, however, is its true line width since the modulation is much smaller than the observed value.

associated with the growth of the $C_{60}^{\bullet +}$ (band b), and when disproportionation of $^3C_{60}$ was not feasible (vide infra) in benzene or in toluene at $T < 200$ K, only the band a can be observed.

Band b has essentially the same g and ΔH_{pp} values as those of $C_{60}^{\bullet +}$ cation radical produced by chemical oxidation of C_{60} by fuming sulfuric acid.[12] The quenching and subsequent disappearance of band b upon addition of 6% methanol or the presence of 12% benzonitrile strongly indicates the electron deficient character of band b. Miller et al. reported that nucleophiles, such as methanol and 1-butanol, attack $C_{60}^{\bullet +}$ and generate multiple addition adducts.[13] Dubois et al. also reported that in benzonitrile the oxidation of C_{60} to $C_{60}^{\bullet +}$ is irreversible.[2b] Based on these features, band b was assigned to be the $C_{60}^{\bullet +}$ cation radical. Although the g values of alkyl substituted C_{60} free radicals[14] is also at 2.0024, band b is unlikely to be due to alkyl substituted C_{60} free radicals. In our system, no alkyl radical is expected to be generated at the early time scale. In addition, the well defined hyperfine splitting of alkyl substituted C_{60} free radical was not observed. Most importantly, alkyl substituted C_{60} free radical will not disappear in the presence of either methanol or benzonitrile.

In a time resolved ESR study, Levanon et al.[6c] observed a narrow band of $g = 2.0016$ at the μs time scale and assigned it to be the delocalized electron in a $[C_{60}^{+}, e^{-}]$ loose ion pair within C_{60} aggregates. The proposal, however, is ambiguous. Electron transfer between $^3C_{60}$ and C_{60} is energetically highly disfavored ($\Delta G = +1.27$ eV, vide infra) and will not occur. In the current system, both bands a and b were still observed under either low dose irradiation (100 W) or dilute (0.05 mM) concentration, where the formation of C_{60} aggregates is much less favored. Besides, the delocalized electron in C_{60} aggregates (i.e., intermolecularly delocalized $C_{60}^{\bullet -}$ anion radical) will not disappear in the presence of either methanol or benzonitrile. Therefore, the possibility of band b being due to the delocalized electron in the $[C_{60}^{+}, e^{-}]$ loose ion pair within C_{60} aggregates was excluded.

Band b is somehow related to the other band b′. In the presence of the organic salt, band b disappears and band b′ appears instead. Band b′ can be quenched by the presence of methanol, the same as band b. We therefore assign band b′ as the $C_{60}^{\bullet +}$ cation radical. The g value of the band b′, however, is different from that of band b, which is attributed to the electrostatic interaction between $C_{60}^{\bullet +}$ and the $(ph)_4B^{-}$ anion. The electrostatic field induced Δg shift of 0.0017 for $C_{60}^{\bullet +}$ cation radical is not unreasonable. In literature, the reported g value ranges from 1.998 to 2.001 for electrochemically generated $C_{60}^{\bullet -}$ in complexation with various cationic counter part of organic salts,[15,16] and the electrostatic field induced Δg shift of 0.003 is much larger than that of the $C_{60}^{\bullet +}$ cation radical reported here.

Concerning the identity of broad band c, its g value, ΔH_{pp}, and ionic character are all consistent with those of $C_{60}^{\bullet -}$ anion radical. The characteristic broad line width of the $C_{60}^{\bullet -}$ anion radical is not commonly observed for organic radicals and has been rationalized to be due to thermally activated redistribution among Jahn-Teller sublevels.[16] The observed ΔH_{pp} value of band c seems to be different from that of the $C_{60}^{\bullet -}$−tetraphenylphosphonium complex in *o*-dichlorobenzene.[15a] The difference in the ΔH_{pp} value is attributed to the solvent effect. In literature, the reported g and ΔH_{pp} values of $C_{60}^{\bullet -}$ are quite different and are strongly solvent and counter ion dependent.[16] For example, when forming complexes with tetrabutylammonium cation in pyridine, the ΔH_{pp} of $C_{60}^{\bullet -}$ becomes ~50 G at 210 K.[16] Nevertheless, the common features of the $C_{60}^{\bullet -}$ anion radical are the very broad line width and the inverse linear line width dependence on the temperature in the 100−300 K region.[15a,16] To further confirm our assignment, the temperature dependence of the line width of band c was measured and shown in Figure 3. As expected, the ΔH_{pp} of the band c decreases almost linearly to 4 G at 77 K, well matching the reported characteristic behavior of the $C_{60}^{\bullet -}$ anion radical. The Arrhenius plot of the increase in the line width gives an activation energy of 0.037 eV for the thermally activated Jahn-Teller sublevels. This value is also within the reported range for $[C_{60}^{\bullet -}$ counterion] complexes in various solvent systems.[16] Therefore, band c is assigned to be the $C_{60}^{\bullet -}$ in the complex form with its cationic counter part.

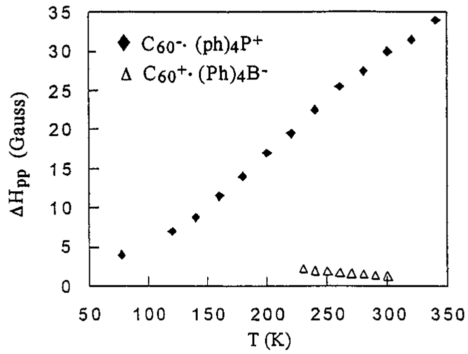

Figure 3. The peak to peak line width, ΔH_{pp}, of both $C_{60}^{\bullet -}$ and $C_{60}^{\bullet +}$ ion radicals as a function of temperature. The condition of the solution is the same as in Figure 2(g).

How were the $C_{60}^{\bullet +}$ and $C_{60}^{\bullet -}$ ion radicals formed? The formation of these two ion radicals is attributed to the disproportionation of two $^3C_{60}$. The free energy for the disproportionation process of photoexcited triplet C_{60} molecules was considered as follows. The first oxidation and the first reduction potentials of ground state C_{60} are +1.76 and −0.43 V_{SCE}, respectively.[2] The lowest triplet energy of C_{60} in toluene is 1.57 eV.[17] The redox potentials of excited state donor (*D) and acceptor (*A) can be obtained according to $E_{1/2}(^*D) = E(D/D^{+}) - E_{0,0}$ (D) and $E_{1/2}(^*A) = E_{1/2}(A^{-}/A) + E_{0,0}(A)$, where $E_{0,0}$ is the excited state energy.[18] Therefore, the first oxidation and reduction potentials of $^3C_{60}$ were calculated to be +0.19

---

[12] Thomann, H.; Bernardo, M.; Miller, G. P. *J. Am. Chem. Soc.* **1992**, *114*, 6593.

[13] Miller, G. P.; Hsu, C. S.; Thomann, H.; Chiang, L. Y.; Bernardo, M. *Mater. Res. Soc. Symp. Proc.* **1992**, *247*, 293.

[14] (a) Krusic, P. J.; Wasserman, E.; Parkinson, B. A.; Malone, B.; Holler, E. R., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 6274. (b) Morton, J. R.; Preston, K. F.; Krusic, P. J.; Hill, S. A.; Wasserman, E. *J. Phys. Chem.* **1992**, *96*, 3576. (c) Krusic, P. J.; Rae, D. C.; Johnston, E.; Morton, J. R.; Preston, K. F.; *J. Phys. Chem.* **1993**, *97*, 1736. (d) Fagan, P. J.; Krusic, P. J.; McEwen, C. N.; Lazar, J.; Parker, D. H.; Herron, N.; Wasserman, E. *Science* **1993**, *262*, 404.

[15] (a) Allemand, P. M.; Srdanov, G.; Koch, A.; Khemani, K.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 2780. (b) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364. (c) Penicaud, A.; Hsu, J.; Reed, C. A.; Koch, A.; Khemani, K. C.; Allemand, P. M.; Wudl, F. *J. Am. Chem. Soc.* **1991**, *113*, 6698. (d) Greaney, M. A.; Gorun, S. M. *J. Phys. Chem.* **1991**, *95*, 7142. (e) Chen, J.; Huang, Z. E.; Cai, R. F.; Shao, G. F.; Chen, S. M.; Ye, H. J. *J. Chem. Soc. Chem. Comm.* **1994**, 2177. (f) Moriyama, H.; Kobayashi, H.; Kobayashi, A.; Watanabe, T. *J. Am. Chem. Soc.* **1993**, *115*, 1185. (g) Subramanian, R.; Booulas, P.; Vijayashree, M. N.; D’Souza, F.; Jones, M. T.; Kadish, K. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1847. (h) Pénicaud, A.; Benítez, A. P.; Gleason, R.; Munoz, V. E.; Escudero, R. *J. Am. Chem. Soc.* **1993**, *115*, 10392. (i) Stinchcombe, J.; Penicaud, A. Bhyrappa, P. Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 5212.

[16] Dubois, D.; Jones, M. T.; Kadish, K, M. *J. Am. Chem. Soc.* **1992**, *114*, 6446.

[17] (a) Hung, R. R.; Grabowski, J. J. *J. Phys. Chem.* **1991**, *95*, 6073. (b) Zeng, Y.; Biczok, L.; Linschitz, H. *J. Phys. Chem.* **1992**, *96*, 5237.

[18] Kavarnos, G. J. In *Photoinduced Electron Transfer I*; Mattay, J., Ed.; Springer-Verlag: Berlin, 1990; Vol. 156, pp 21−58.

and $+1.14\ V_{SCE}$, respectively. The Gibbs free energy for the disproportionation process of excited state molecules can be estimated by the Rehm-Weller eq[19] (eq 1),

$$\Delta G = E_{1/2}(^*\mathrm{D}) - E_{1/2}(^*\mathrm{A}) + E_{\mathrm{coul}} \qquad (1)$$

where E_{coul} = Coulomb interaction energy = $(e^2N/4\pi\epsilon_0 a) \times [1/\epsilon - 2/37.5]$.[20] By substituting the dielectric constant ϵ of 2.44 for toluene, and a of 7 Å for the encounter distance (between cationic and anionic sites) into eq 1, one estimates the free energy ΔG of -0.2 eV for the disproportionation process of triplet C_{60} molecules in toluene (see eq 2). That is,

$$^3C_{60} + {}^3C_{60} \rightarrow C_{60}^{\bullet+} + C_{60}^{\bullet-} \quad \Delta G \approx -0.2 \text{ eV (in toluene)} \qquad (2)$$

disproportionation of two $^3C_{60}$ indeed can occur in toluene. Similar to the triplet state, disproportionation of excited singlet C_{60} is also thermodynamically allowed. However, the disproportionation of excited singlet C_{60} is likely to occur in the solid phase but not in the solution phase due to its short lifetime (1.2 ns)[21] and therefore the very limited encountering probability of two singlet C_{60}. The electron transfer between the triplet C_{60} and the ground C_{60} is energetically highly disfavored ($\Delta G = +1.27$ eV) and therefore will not occur. The fact that disproportionation of $^3C_{60}$ is so sensitive to temperature in the 200−330 K region indicates that the free energy for eq 2 must be smaller in magnitude than the estimated value (i.e., a less negative value). Therefore, in a less polar solvent, benzene (ϵ = 2.28), the disproportionation of $^3C_{60}$ becomes not feasible,[22] and only the $^3C_{60}$ band was observed. Disproportionation is not a unique property of excited state fullerene molecules but a common feature of a lot of compounds under intense photoirradiation.[23] As long as twice the amount of the excitation energy is enough to compensate for the energy gap between the reduction and the oxidation potentials of a ground state molecule as well as the solvent reorganization energy, disproportionation of any excited state molecules is always feasible.

The activation energy, E_a, for the disproportionation process of $^3C_{60}$ can be obtained from the plot of the ESR intensity of $C_{60}^{\bullet+}$ vs the reciprocal of temperature. To correct the temperature (T^{-1}) dependence of the ESR intensity (the Curie's law, $I = C/T$), the ESR intensity[24] of the $C_{60}^{\bullet+}$ was multiplied by T and plotted vs $1/T$. An activation energy E_a of ~0.15 eV was obtained for the disproportionation reaction of triplet C_{60} molecules (see Figure 4).

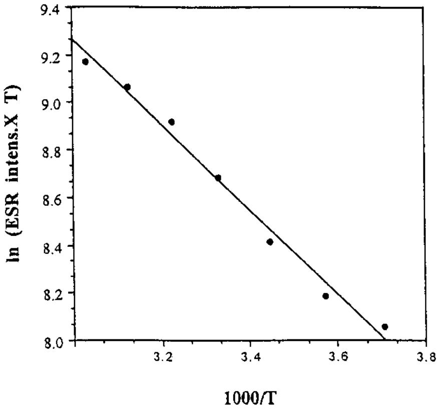

Figure 4. Arrhenius plot of natural logarithm of ($C_{60}^{\bullet+}$ ESR intensity × T) vs $1/T$. The solution is 2 mM C_{60} in toluene.

The $C_{60}^{\bullet-}$ anion radical was not observed in the absence of the organic salt, which could be due to the broad line width and the short T_2 relaxation time of $C_{60}^{\bullet-}$.[25a] Another alternative for the absence of the $C_{60}^{\bullet-}$ anion radical could possibly be the coupling reaction between two $C_{60}^{\bullet-}$ to form the ESR silent $(C_{60})_2^{2-}$ dimer dianion, as suggested by Eaton and co-workers.[25b] Formation of a C−C bond will release 35 kcal/mol energy. The back electron transfer between $C_{60}^{\bullet-}$ to $C_{60}^{\bullet+}$ also reduces the steady state concentration of these two species. The steady state ESR intensity is inversely proportional to the lifetime of the transient species. In the presence of the $(ph)_4P^+(ph)_4B^-$ organic salt, the $C_{60}^{\bullet-}$ anion radical appears. The effect of the organic salt can be well understood in terms of inhibiting the back electron transfer, forming complexes with $C_{60}^{\bullet-}$, and therefore prolonging the lifetimes of the ion radicals. It was reported before that organic salts were able to retard the back electron transfer rate between donor and acceptor ion radicals in several systems.[26]

Below 200 K, only band a was observed in toluene, and the solution remains a purple color after a long period of time of irradiation (> 3 h). At high temperatures (e.g., 300 K), irradiation of the C_{60} solution causes slow conversion of the purple colored solution to the formation of brown precipitates. Whereas in benzene, only $^3C_{60}$ can be observed, and the solution remains purple after a long time of irradiation at all temperatures (180−330 K). The conversion of C_{60} to the brown precipitates is strongly associated with the presence of $C_{60}^{\bullet+}$ (and/or the $C_{60}^{\bullet-}$ anion radical) and is accelerated by high temperatures in toluene. The formation of brown precipitates resembles the "photodegradation" of fullerene solution reported in literature.[7−9] Desorption chemical ionization (DCI) mass measurements of the brown toluene solution reveals the addition of several solvent (toluene) molecules to the fullerene cage (see Figure 5). Similar solvent addition to the fullerene cage was observed by Schuster and co-workers[4c] in the photolysis of C_{60}−9,10-dicyanoanthracene−toluene solution. They proposed the formation of the $C_{60}^{\bullet+}$ cation radical, which then abstracts the methyl hydrogen atom from the solvent. In a cyclic voltametry study, Guarr and co-workers[27] found that $C_{60}H_2$ undergoes irreversible oxidation by stepwisely losing two electrons and two protons to produce C_{60}. That is, $C_{60}H^{\bullet+}$ cation radical favors to release a proton

---

[19] (a) Rehm, D.; Weller, A. *Israel J. Chem.* **1970**, *8*, 259. (b) Weller, A. *Z. Phys. Chem. NF* **1982**, *133*, 93.

[20] Mattay, J.; Runsink, J.; Gersdorf, J.; Rumbach, T.; Ly, C. *Helv. Chim. Acta* **1986**, *69*, 442.

[21] Kim, D.; Lee, M.; Suh, Y. D.; Kim, S. K. *J. Am. Chem. Soc.* **1992**, *114*, 4429.

[22] A referee questioned whether the slight change in the solvent dielectric constant from 2.44 (toluene) to 2.28 (benzene) can hinder the disproportionation process. The experimental fact is that photolysis of C_{60} in benzene within temperature range of 180−330 K affords only the $^3C_{60}$ band as the sole observed signal. Alternative possibility is that two $^3C_{60}$ do undergo disproportionation process, and the $C_{60}^{\bullet+}$ cation radical disappears completely by reacting with the bulk solvent, as does with toluene and benzonitrile. To test this possibility, C_{60} in benzene was photolyzed by UV−visible light (500 W) for 10 h, and the DCI mass spectrum of the remained purple solution was measured. No C_{60}−benzene adduct was observed from the mass analysis. Therefore, the change in the solvent dielectric constant (and thus the free energy ΔG) is most probably responsible for the absence of disproportionation of $^3C_{60}$ in benzene.

[23] Mauzerall, D.; Ballard, S. G. *Ann. Rev. Phys. Chem.* **1982**, *33*, 377.

[24] Since the right part of the $C_{60}^{\bullet+}$ band overlaps with the left part of $^3C_{60}$, only the area of the left part of the $C_{60}^{\bullet+}$ band was integrated and used in the Arrhenius plot.

[25] (a) Schell-Sorokin, A. J.; Mehran, F.; Eaton, G. R.; Eaton, S. S.; Viehbeck, A.; O'Toole, T. R.; Brown, C. A. *Chem. Phys. Lett.* **1992**, *195*, 225. (b) Khaled, M. M.; Carlin, R. T.; Trulove, P. C.; Eaton, G. R.; Eaton, S. S. *J. Am. Chem. Soc.* **1994**, *116*, 3465.

[26] (a) Rabani, J.; Sassoon, R. R. *J. Phys. Chem.* **1990**, *84*, 1319. (b) Santamaria, J. In *Photoinduced Electron Transfer*; Fox, M., Chanon, M., Eds., Elsevier: Amsterdam, 1988; Part B, pp 483−540. (c) Kawanishi, Y.; Kitamura, N.; Tzuke, S. *J. Phys. Chem.* **1986**, *90*, 6034. (d) Goodson, B.; Schuster, G. B. *Tetrahedron Lett.* **1986**, *27*, 3123.

[27] Guarr, T. F.; Meier, S. M.; Vance, V. K.; Clayton, M. *J. Am. Chem. Soc.* 1**993**, *115*, 9862.

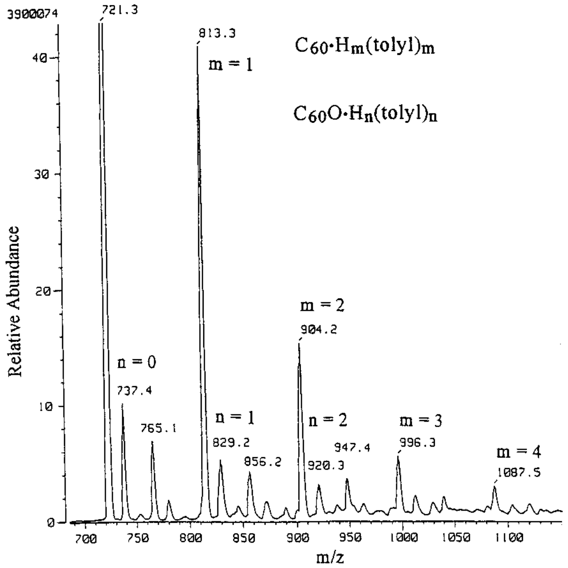

Figure 5. Desorption chemical ionization (DCI) mass spectrum of the solution part of a C_{60} (2 mM)−toluene solution irradiated by UV−visible light (500 W) for 2 h.

or a hydrogen atom to generate C_{60} or $C_{60}^{\bullet+}$ cation radical. Bard and co-workers[28] also found that electrochemically generated $C_{60}^{\bullet-}$ does not combine with a proton in the bulk solution. Therefore, it is very unlikely that $C_{60}^{\bullet+}$ cation radical will abstract a methyl hydrogen atom from the toluene solvent. Besides, it is well-known in organic textbooks that alkyl cations undergo electrophilic addition to a benzene ring. We therefore believe the more likely mechanism being that the $C_{60}^{\bullet+}$ radical cation undergoes Friedel−Crafts type of addition to the para position of toluene, instead of hydrogen abstraction from the methyl proton of toluene. In fact, the coupling of several benzene molecules to both C_{60} and halogenated C_{60} in the presence of $AlCl_3$ was reported before.[29] Besides the $C_{60}{\cdot}H_m(\text{tolyl})_m$ ($m = 1-4$) adducts, the $C_{60}O{\cdot}H_n(\text{tolyl})_n$ ($n = 0-2$) adducts were also observed as minor products (Figure 5). The small amount of oxygen atom probably was introduced during the mass measurements since the $C_{60}O$ adduct was very often observed as trace impurity in the DCI-MS spectrum. Fast atomic bombardment (FAB) mass measurement of the brown precipitate shows the presence of C_{60} dimer and trimers.[30] We believe that disproportionation and subsequent coupling between $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ could be another important route responsible for the solid phase polymerization, in addition to the previously proposed [2 + 2] cycloaddition mechanism.[31]

Besides the photopolymerization of C_{60} solid thin film, disproportionation of $^3C_{60}$ is also related to the laser light dependent triplet lifetime[32] of C_{60}. In addition to the triplet−triplet annihilation[6b] process, the formation of both $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ provide additional channels for the relaxation of $^3C_{60}$ (see eq 3 and 4).

$$^3C_{60} + C_{60}^{\bullet+} \rightarrow C_{60}^{\bullet+} + C_{60} \quad \Delta G = -1.57\ \text{eV} \tag{3}$$

$$^3C_{60} + C_{60}^{\bullet-} \rightarrow C_{60}^{\bullet-} + C_{60} \quad \Delta G = -1.57\ \text{eV} \tag{4}$$

Quenching of $^3C_{60}$ by both $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ are strongly thermodynamically allowed and release 1.57 eV free energy. Photoirradiation of C_{70} in solution also exhibits disproportionation behavior.

In literature, there are still many other measurements concerning the nonlinear photochemical properties of C_{60} solution or thin films, such as nonlinear photoconductivity,[33] nonlinear optical property,[34] optical limiting,[35] delayed photoionization,[36] photocoalescence of fullerenes,[37] etc. These phenomena largely rely on the dipole changes and/or charge formation of systems and were observed under intense photoirradiation conditions. Therefore, the formation of fullerene cation and anion radicals could be, at least partly, responsible for these nonlinear properties of fullerene thin films or solutions.

Conclusion

Disproportionation of photoexcited $^3C_{60}$ has been observed. Theoretical estimation in the free energy also supports the feasibility of this process. Simultaneous observation of both $^3C_{60}$ and $C_{60}^{\bullet+}$ clarifies the previous arguments about the assignment of a single ESR band generated by irradiation of C_{60} solution in time resolved experiments.[6c−f,38] The use of an organic salt, i.e., $(ph)_4P^+(ph)_4B^-$, to stabilize the otherwise unobservable, photochemically generated $C_{60}^{\bullet-}$ anion radical was also demonstrated. Both the previously reported photodegradation of C_{60} solution and laser light dependent C_{60} triplet lifetime can be rationalized by disproportionation of two $^3C_{60}$. We believe that disproportionation of excited state fullerenes molecules is a common process in systems under intense irradiation and could be involved in many other reported photochemical processes, such as, photopolymerization of C_{60} films, nonlinear photoconductivity, nonlinear optical property, optical limiting, delayed photoionization, photocoalescence of fullerenes, etc. It would be necessary to re-evaluate these photochemical phenomena and take into account the crucial roles of fullerene cation/anion radicals as well as their subsequent chemical reactions and products.

Experimental Section

C_{60} (99.9+%) was purchased from the MER corporation (Tucson, AZ). Solvents, such as toluene, benzene, benzonitrile, methanol, were purchased from Aldrich (all spectroscopic grades) and used as received. Tetraphenylphosphonium tetraphenylborate (hereafter, $(ph)_4P^+(ph)_4B^-$, TCI, Japan) was recrystalized from ethanol twice. The quartz ESR tube (Wilmad, 710-SQ) was connected to the head of a J-Yang NMR

---

[28] Cliffel, D. E.; Bard, A. J. *J. Phys. Chem.* **1994**, *98*, 8140.

[29] Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.;Sensharma, D. K.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1991**, *113*, 9385, 9387.

[30] The $(C_{60})_n$ ($n = 2, 3$) mass peaks appear along with a series of regular C_2 addition and elimination peaks. The abundance of $(C_{60})_2$ peak is ∼4% of the 720 amu main peak (or 2 times of the noise level). The formation of $(C_{60})_n$ is probably via the coupling of C_{60} cation and anion radicals, of which the yield is limited by the triplet spin state of the radical ion pair and the competing back electron transfer process.

[31] (a) Rao, A. M.; Zhou, P.; Wang, K. A.; Hager, G. T.; Holden, J. M.; Wang, Y.; Lee, W. T.; Bi, X.; Eklund, P. C.; Cornett, D. S.; Duncan, M. A.; Amster, I. J. *Science* **1993**, *259*, 955. (b) Cornett, D. S.; Amster, I. J.; Duncan, M. A.; Rao, A. M.; Eklund, P. C. *J. Phys. Chem.* **1993**, *97*, 5036.

[32] Kajii, Y.; Nakagawa, T.; Suzuki, S.; Achiba, Y.; Obi, K.; Shibuya, K. *Chem. Phys. Lett.* **1991**, *181*, 100.

[33] (a) Kaiser, M.; Reichenbach, J.; Byrne, H. J.; Anders, J.; Maser, W.; Roth, S.; Zahab, A.; Bernier, P. *Solid State Comm.* **1992**, *81*, 261. (b) Mort, J.; Okumura, K.; Machonkin, M.; Ziolo, R.; Huffman, D. R.; Ferguson, M. I. *Chem. Phys. Lett.* **1991**, *186*, 281.

[34] (a) Yang, L.; Dorsinville, R.; Alfano, R. *Chem. Phys. Lett.* **1994**, *226*, 605. (b) Talapatra, G. B.; Manickam, N.; Samoc, M.; Orczyk, M. E.; Karna, S. P.; Prasad, P. N. *J. Phys. Chem.* **1992**, *96*, 5206. (c) Meth, J. S. Vanherzeele, H.; Wang, Y. *Chem. Phys. Lett.* **1992**, *197*, 26.

[35] Tutt, L. W.; Kost, A. *Nature* **1992**, *356*, 225.

[36] (a) Wurz, P.; Lykke, K. R. *J. Phys. Chem.* **1992**, *96*, 10129. (b) Ding, D.; Compton, R. N.; Haufler, R. E.; Klots, C. E. *J. Phys. Chem.* **1993**, *97*, 2500.

[37] Yeretzian, C.; Hansen, K.; Diederich, F.; Whetten, R. L. *Nature* **1992**, *359*, 44; Beck, R. D.; Weis, P.; Hirsch, A.; Lamparth, I. *J. Phys. Chem.* **1994**, *98*, 9683.

[38] Ruebsam, M.; Dinse, K. P.; Plueschau, M.; Fink, J.; Kraetschmer, W.; Fostiropoulos, K.; Taliani, C. *J. Am. Chem. Soc.* **1992**, *114*, 10059.

tube (Wilmad 528-JY). In general, the C_{60} (2 mM)−toluene solution was deoxygenated by several freeze−pump−thaw cycles and then filled in one atmosphere N_2 gas in the final run. The light source was the output of an Oriel 500 Watt high pressure Hg lamp via a water filter. The C_{60} solution was irradiated in the ESR chamber (Brucker, ER 200D-SRC, Germany) operating at 9.58 GHz, modulation 2.0 G_{pp}, and microwave power of 18 dB in all experiments. The sample temperature was controlled by a Brucker variable-temperature control unit ER4111 VT.

In the case of the presence of organic salts, typically 1.5 mg of $(Ph)_4P^+(Ph)_4B^-$ was added into 0.5 mL C_{60} (2 mM)−toluene solution. The organic salt does not dissolve completely and remains suspended in the solution. During irradiation, the $C_{60}{}^{\bullet-}$ and $C_{60}{}^{\bullet+}$ ion radicals form complexes with their organic salt counterions, respectively, and precipitate down to the bottom of the ESR tube as dark brown solid which is mainly responsible for the observed ESR signal. The upper layer of the solution gradually becomes transparent and only gives weak ESR signal.

Acknowledgment. The authors acknowledge the financial support from the National Science Council of the Republic of China, Grant No. NSC 83-0208-M-007-046.

JA952640L