

## Excited Triplet and Reduced Forms of C<sub>84</sub>

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Received: November 10, 1994<sup>⊗</sup>

The triplet excited state behavior of C<sub>84</sub> has been probed by the triplet–triplet energy transfer method using pulse radiolytically generated biphenyl triplets in benzene. The triplet excited state has a weak absorption in the UV (difference absorption maxima at 310 and 345 nm) but no significant absorption in the visible. The rate constants for energy transfer from <sup>3</sup>BP\* and <sup>3</sup>C<sub>60</sub>\* are  $4 \times 10^9$  and  $4.7 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>, respectively. Triplet excited state properties of <sup>3</sup>C<sub>84</sub>\* are compared with other fullerenes. A photocatalytic method has also been successfully employed to reduce C<sub>84</sub> in a UV-irradiated colloidal TiO<sub>2</sub> suspension.

### Introduction

The photophysical, photochemical, and photoelectrochemical properties of fullerenes, C<sub>60</sub> and C<sub>70</sub>, have been studied extensively over the past couple of years [see, for example, refs 1–26]. The long-lived triplet excited state and absorption in the visible makes fullerenes suitable for photosensitization, singlet oxygen production, and solar energy conversion. Doped polymer films have also been shown to possess photoconductive properties. There is now increasing interest in studying the physical properties of larger fullerenes, C<sub>76</sub>, C<sub>78</sub>, C<sub>82</sub>, C<sub>84</sub>, etc.<sup>27–31</sup> However, little is known regarding the excited state behavior of these larger fullerenes.

C<sub>84</sub> is one of the larger fullerenes produced in abundant quantities during the synthesis of C<sub>60</sub>. Unlike C<sub>60</sub> and C<sub>70</sub>, C<sub>84</sub> exists in two isomers, D<sub>2</sub> and D<sub>2d</sub>, in the ratio 2:1.<sup>27,28</sup> The visible absorption spectra of C<sub>84</sub><sup>29</sup> and the reduction potentials of C<sub>84</sub><sup>27–31</sup> have already been reported. At least six reversible reductions have been characterized using cyclic voltammetry.<sup>27a,b</sup> Although distinctively different electronic properties of these two isomers were observed in electrochemical and ESR studies, the separation of the two isomers of C<sub>84</sub> has not yet been achieved. Consequently, a mixture of the two isomers has been used in this investigation. We report here, for the first time, experimental results which characterize triplet excited state properties of C<sub>84</sub>. We also report the photoelectrochemical reduction of C<sub>84</sub> in colloidal TiO<sub>2</sub> suspension.

### Experimental Section

**Materials.** Mass-pure C<sub>84</sub> was obtained via selective solvent extraction followed by HPLC chromatography with a semi-preparative Buckyclutcher column (Regis) run in recycling mode. Details of the selective solvent enrichment techniques will be published later.<sup>26a</sup> The purity of the sample was checked by surface analysis via laser ionization (SALI) mass spectrometry (MS), a technique that has been used extensively at SRI International for analysis of fullerene samples.<sup>27b</sup> SALI-MS showed that the fullerene purity exceeded 99.5%, with the only impurity peaks belonging to C<sub>82</sub> and C<sub>86</sub>; in particular, no C<sub>60</sub> or C<sub>70</sub> was present in the SALI-MS spectrum obtained. The

sample was washed with diethyl ether three times and then dried for a period of 48 h in a vacuum oven held at 343 K.

**Optical Measurements.** Absorption spectra were recorded with a Perkin-Elmer 3840 diode array spectrophotometer. Nanosecond laser flash photolysis experiments were carried out with a Laser Photonics PRA/Model UV-24 nitrogen laser system (337 nm, 2 ns pulse width, 2–4 mJ/pulse) with a front face excitation geometry. A typical experiment consisted of a series of 2–3 replicate shots per single measurement. The average signal was processed with an LSI-11 microprocessor interfaced with VAX-3400 computer. Details of the experimental setup can be found elsewhere.<sup>32a</sup>

Pulse radiolysis experiments were performed at 296 K with the Notre Dame 7 MeV ARCO LP-7 linear accelerator, the operating conditions of which are described elsewhere.<sup>32b</sup> The dose per pulse was in the range 1–5 Gy, determined by thiocyanate dosimetry. The solutions were saturated with nitrogen or oxygen and flowed continuously during the experiment.

### Results and Discussion

The absorption spectrum of C<sub>84</sub> in toluene is compared to that of C<sub>60</sub> in Figure 1. While the solution of C<sub>60</sub> is purple, the solutions of C<sub>84</sub> exhibit yellow-green color. The C<sub>84</sub> exhibits significantly stronger absorption in the visible. The details of the structural and electronic properties of the C<sub>84</sub> are presented elsewhere.<sup>29</sup> Direct excitation of C<sub>84</sub> via nanosecond laser flash photolysis using 337 nm excitation wavelength (2 mJ/pulse) did not yield a conclusive spectrum of <sup>3</sup>C<sub>84</sub>\*; the transient absorbance in the UV–visible region was very low (<0.002).<sup>33</sup> This observation indicates that either the intersystem crossing efficiency for the <sup>3</sup>C<sub>84</sub>\* generation is very low or the triplet excited state has a very low extinction coefficient in the UV–visible region. An alternate route of triplet–triplet energy transfer was therefore employed to generate <sup>3</sup>C<sub>84</sub>\*.

**Pulse Radiolysis Experiments.** Radiolysis of a benzene solution containing a high concentration of biphenyl is known to yield relatively long-lived excited biphenyl triplet with absorption maximum at 360 nm. The resulting biphenyl triplets are capable of transferring energy to a molecule with a lower triplet energy. This technique has been successfully used by us and others to generate <sup>3</sup>C<sub>60</sub>\* and <sup>3</sup>C<sub>70</sub>\*.<sup>6a,9,10</sup> The absorbed doses were in the range 4–20 Gy/pulse. The experiments were carried out with a continuous flow of the sample solution.

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<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, February 1, 1995.

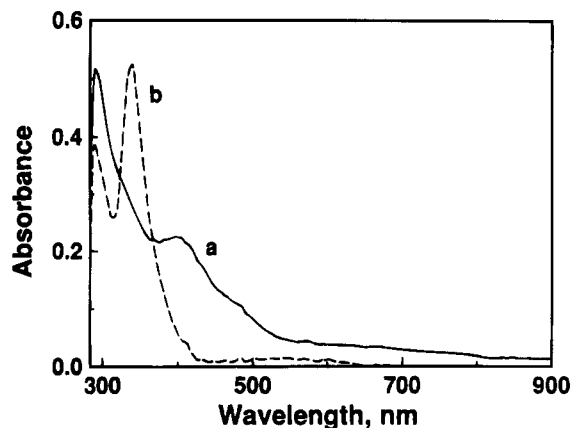


Figure 1. Absorption spectra of (a) 10  $\mu\text{M}$  C<sub>84</sub> and (b) 6.5  $\mu\text{M}$  C<sub>60</sub> in toluene.

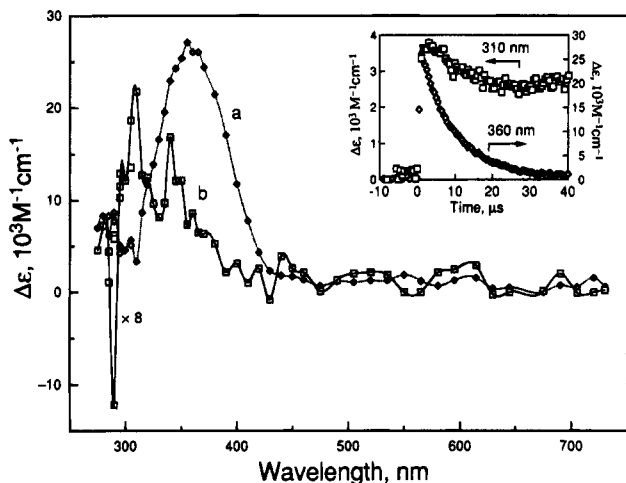
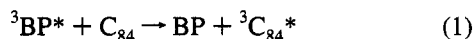


Figure 2. Transient absorption spectra obtained (a) 1  $\mu\text{s}$  (<sup>3</sup>BP\*) and (b) 35  $\mu\text{s}$  (<sup>3</sup>C<sub>84</sub>\*) after pulse radiolysis of deaerated benzene solution containing 0.05 M biphenyl and 10  $\mu\text{M}$  C<sub>84</sub>. Inset shows normalized decay traces recorded at 360 and 310 nm corresponding to the transients <sup>3</sup>BP\* and <sup>3</sup>C<sub>84</sub>\*, respectively.

The biphenyl triplet is relatively short-lived in the presence of C<sub>84</sub> as a result of the T–T energy transfer process (reaction 1).



The bimolecular rate constant for the quenching of biphenyl triplet by C<sub>84</sub> was  $4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . This value, which is close to a diffusion-controlled process, is slightly lower than the values of  $1.7 \times 10^{10}$  and  $2.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  for energy transfer to C<sub>60</sub> and C<sub>70</sub>, respectively.<sup>6a</sup> In the absence of C<sub>84</sub>, <sup>3</sup>BP\* is the only species generated in the pulse radiolysis experiment. However, in the presence of C<sub>84</sub>, transients with two different lifetimes were evident. This is clearly evident from the absorption–time profiles recorded in the presence of C<sub>84</sub> (inset in Figure 2).

The transient absorption spectra obtained after 1 and 35  $\mu\text{s}$  are shown in Figure 2. While the transient absorption spectrum recorded at short times (spectrum a) corresponds to <sup>3</sup>BP\*, the transient absorption spectrum recorded at longer times (spectrum b) corresponds to <sup>3</sup>C<sub>84</sub>\*. The difference absorption spectrum of <sup>3</sup>C<sub>84</sub>\* exhibits maxima at 310 and 345 nm. The maximum bleaching observed at 290 nm corresponds to the ground state maximum in this region. It has been shown earlier that <sup>3</sup>C<sub>60</sub>\* has significant absorptions in the visible,<sup>1–10</sup> but surprisingly, <sup>3</sup>C<sub>84</sub>\* does not exhibit any noticeable absorption in the visible

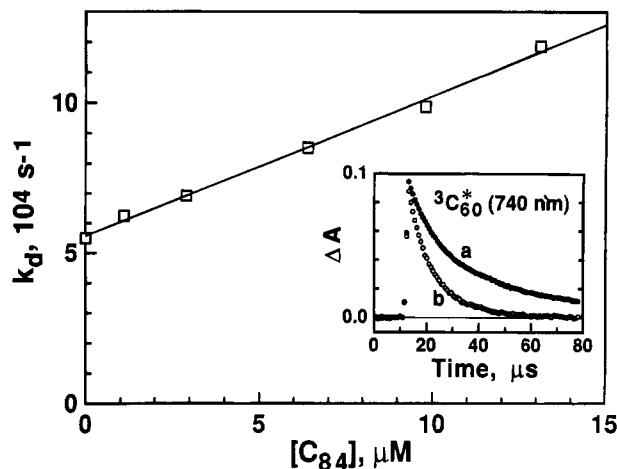


Figure 3. Dependence of pseudo-first-order decay rate constant of <sup>3</sup>C<sub>60</sub>\* on the concentration of C<sub>84</sub>. Inset shows the decay of <sup>3</sup>C<sub>60</sub>\* at 740 nm: (a) in the absence and (b) in the presence of 135  $\mu\text{M}$  C<sub>84</sub>.

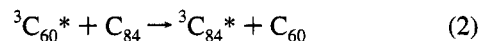
TABLE 1: Triplet Excited State Properties of Fullerenes

	C <sub>60</sub> <sup>a</sup>	C <sub>70</sub> <sup>a</sup>	C <sub>84</sub> <sup>b</sup>
abs max, nm	400, 740	435, 970	310
extinction coefficient, M <sup>-1</sup> cm <sup>-1</sup>	6600, 16000	9000, 4000	4430
lifetime, $\mu\text{s}$	250	250	<100
$k(^3\text{C}_{60}^*)$ , <sup>c</sup> 10 <sup>9</sup> M <sup>-1</sup> s <sup>-1</sup>	0.2	2.4	4.7

<sup>a</sup> In benzene or toluene (compiled from refs, 6a, 10b, 11a, and 12b). <sup>b</sup> In benzene (present study). <sup>c</sup> Bimolecular rate constant for the quenching of <sup>3</sup>C<sub>60</sub>\* by the corresponding fullerene.

region. By using the expression for energy transfer method,<sup>34</sup> we estimate the maximum extinction coefficient of <sup>3</sup>C<sub>84</sub>\* at 310 nm to be  $4430 \text{ M}^{-1} \text{ cm}^{-1}$ . (The value of  $27\,100 \text{ M}^{-1} \text{ cm}^{-1}$  was used as  $\epsilon_d$  for <sup>3</sup>BP\* at 360 nm.)<sup>34</sup>

**Energy Transfer between <sup>3</sup>C<sub>60</sub>\* and C<sub>84</sub>.** Triplet–triplet energy transfer between <sup>3</sup>C<sub>60</sub>\* and C<sub>84</sub> was probed by laser flash photolysis. The absorption–time profiles of <sup>3</sup>C<sub>60</sub>\* at 740 nm recorded in the presence and absence of C<sub>84</sub> (inset of Figure 3) show that C<sub>84</sub> is able to quench the triplet excited state of C<sub>60</sub> via T–T energy transfer process (reaction 2).

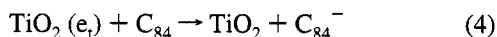
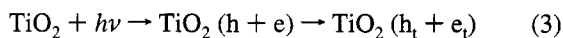


The quenching of <sup>3</sup>C<sub>60</sub>\* by C<sub>84</sub> was monitored from the absorption decay at 740 nm by varying the concentration of C<sub>60</sub>. The dependence of the pseudo-first-order rate constant of <sup>3</sup>C<sub>60</sub>\* decay on the C<sub>84</sub> concentration is shown in Figure 3. The bimolecular rate constant for the quenching of <sup>3</sup>C<sub>60</sub>\* by C<sub>84</sub> determined from the slope of this plot is  $4.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . This value is similar to the one reported for the quenching of <sup>3</sup>C<sub>60</sub>\* by C<sub>70</sub> ( $2.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ).<sup>12b</sup> The nearly diffusion-controlled quenching rate constant observed in the present set of experiments suggests that the triplet energy of C<sub>84</sub> is lower than that of <sup>3</sup>C<sub>60</sub>\*. Strong ground state absorption of C<sub>60</sub> and C<sub>84</sub> and weak absorption of <sup>3</sup>C<sub>84</sub>\* limited the resolution of transient absorption measurements in the UV region.

**Comparison of <sup>3</sup>C<sub>84</sub>\* Properties with Other Fullerenes.** The absorption properties of <sup>3</sup>C<sub>84</sub>\* are compared with other fullerene triplets in Table 1. The only spectral features in the difference absorption spectrum of <sup>3</sup>C<sub>84</sub>\* that are prominent are the absorption bands at 310 and 345 nm. The absence of a major absorption band of triplet excited C<sub>84</sub> in the visible suggests a close match between the ground and excited state spectra. Of all the fullerenes that have been investigated to date, only triplet C<sub>60</sub> is known to exhibit a prominent 740 nm absorption band with a significantly higher extinction coefficient

of  $14\,000\text{ M}^{-1}\text{ cm}^{-1}$ .<sup>11a</sup> However, triplet  $\text{C}_{70}$  exhibits relatively weak absorption bands in the visible. These observations suggest that visible absorption bands are less prominent for triplet excited states of higher fullerenes. However, all of these excited fullerenes are long-lived with intrinsic decay lifetimes greater than  $100\ \mu\text{s}$ . Self-quenching processes such as T-T annihilation and ground state quenching often accelerate the deactivation of the triplet excited state. Another interesting aspect involves energy transfer between two different fullerene molecules. The bimolecular rate constant for the quenching of  ${}^3\text{C}_{60}^*$  by a fullerene molecule increases with increasing number of carbon atoms in the unexcited fullerene molecule (Table 1). If we attribute this increase in the quenching rate constant to the increasing energy gap between the donor and acceptor triplets, it is evident that larger fullerenes have lower triplet energies. A decrease in the energy of the lowest unoccupied molecular orbitals of the fullerenes has also been observed in the electrochemical reduction of larger fullerenes.<sup>27c</sup>

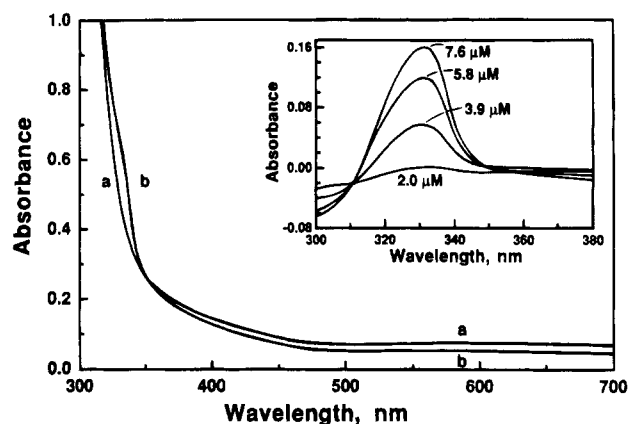
**Reduction of  $\text{C}_{84}$  in Colloidal  $\text{TiO}_2$  Suspension.** Controlled reduction of fullerenes has also been a topic of immense interest in recent years. Up to six reversible reductions have been reported for  $\text{C}_{84}$ .<sup>27b,31</sup> We have now employed a photoelectrochemical approach to reduce  $\text{C}_{84}$  in preirradiated colloidal  $\text{TiO}_2$  suspension (reactions 3 and 4).



The ability of semiconductor clusters to carry out controlled one-electron reduction of  $\text{C}_{60}$  and  $\text{C}_{70}$  under UV excitation has been demonstrated earlier.<sup>35,36</sup> The semiconductor  $\text{TiO}_2$  should be an excellent choice to carry out one-electron reduction of  $\text{C}_{84}$  since the energy of its conduction bands ( $E_{\text{CB}} = -0.5\text{ V}$  vs NHE at pH 7) thermodynamically favors one-electron reduction ( $E^0(\text{C}_{84}/\text{C}_{84}^-) \approx -0.08\text{ V}$  vs NHE).

A deaerated suspension of colloidal  $\text{TiO}_2$  (10 mM) in 50/50 toluene/ethanol was preirradiated with a 1000 W xenon/mercury lamp to induce charge separation followed by trapping of holes ( $h_t$ ) and electrons ( $e_t$ ) within the semiconductor colloids (reaction 3). The solution turned blue as the UV irradiation was continued for 3–5 min. This blue coloration of the colloidal suspension is a characteristic feature of trapped electrons in  $\text{TiO}_2$  colloids.<sup>36</sup> An aliquot ( $40\ \mu\text{L}$ ) of deaerated  $\text{C}_{84}$  solution in toluene ( $2 \times 10^{-4}\text{ M}$ ) was then added to both sample and reference cells (total volume 1 mL). Absorption spectra recorded before and after the addition of  $\text{C}_{84}$  are shown in Figure 4. A cell containing only 50/50 toluene/ethanol solvent mixture was used as the reference. The spectrum recorded after the addition of  $\text{C}_{84}$  (spectrum b in Figure 4) shows a decreased absorption at 700 nm and an increased absorption around 330 nm. The decrease in the absorption at 700 nm indicates that the trapped electrons are scavenged by  $\text{C}_{84}$  to produce  $\text{C}_{84}^-$  (reaction 3). It should be noted that the trapped electrons in a preirradiated  $\text{TiO}_2$  suspension are relatively long-lived and do not disappear without the addition of  $\text{C}_{84}$ .

The spectral features of  $\text{C}_{84}^-$  were further probed by subtracting the contribution of  $\text{TiO}_2$  absorption to the overall spectrum. The difference absorption spectra recorded after each incremental addition of  $\text{C}_{84}$  solution show increased absorption at 330 nm with increasing  $\text{C}_{84}$  concentration (inset of Figure 4). Bleaching around 300 nm further confirms the disappearance of  $\text{C}_{84}$  to form  $\text{C}_{84}^-$ . The disappearance of  $\text{C}_{84}$  cannot be attributed to direct photolysis of  $\text{C}_{84}$  since the  $\text{TiO}_2$  suspension was irradiated with UV light before the addition of  $\text{C}_{84}$ . These observations demonstrate the feasibility of carrying out one-



**Figure 4.** Absorption spectra of 10 mM  $\text{TiO}_2$  colloidal in 50/50 toluene/ethanol (path length = 2 mm, volume = 1 mL) (a) after UV illumination for 3 min and (b) after addition of  $\text{C}_{84}$  to the preirradiated  $\text{TiO}_2$  suspension ( $[\text{C}_{84}] = 7.6\ \mu\text{M}$ ). Inset shows the difference absorption spectra of  $\text{C}_{84}^-$ . The spectra were recorded following the addition of various amounts of  $\text{C}_{84}$  and corrected for the absorbance of  $\text{TiO}_2$  colloids.

electron reduction of  $\text{C}_{84}$  with semiconductor colloids. Further experiments are underway to explore the role of excited  $\text{C}_{84}$  in its participation in the photochemical reactions.

**Acknowledgment.** The work described herein was supported by the Office of Basic Energy Sciences of the U.S. Department of Energy. This is Contribution No. NDRL-3734 from the Notre Dame Radiation Laboratory. We gratefully acknowledge Filipe Chibante for purifying  $\text{C}_{84}$  and Chris Becker for running the SALI-MS analysis of the  $\text{C}_{84}$  sample used in this study.

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JP9427140