

# Oxidation of Triplet C<sub>60</sub> by Hydrogen-Bonded Chloranil: Efficient Formation, Spectrum and Charge-Shift Reactions of C<sub>60</sub><sup>+•</sup> Cation Radical

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The rate of oxidative quenching of <sup>3</sup>C<sub>60</sub> by chloranil (CA) in CH<sub>2</sub>Cl<sub>2</sub> is much enhanced by added trifluoroacetic acid (TFA) or hexafluoro-2-propanol (HFIPA). These additives have similar hydrogen-bonding powers but differ widely in their proton acidities. In both cases, quenching rate constants calculated for H-bonded CA increase sharply with additive concentration. H-bonded clusters around the quinone are postulated in which electron transfer is coupled to fast protonation of CA<sup>-•</sup> by TFA, and strong H-bonding or solvation of charged radicals by HFIPA. This is consistent with observed neutral semiquinone formation, higher radical yields, and much slower back reactions for TFA. The C<sub>60</sub><sup>+•</sup> spectrum ( $\epsilon = 25\,000 \pm 2000 \text{ M}^{-1} \text{ s}^{-1}$  at 980 nm) shows low absorption throughout the visible region. Charge-shift reactions of C<sub>60</sub><sup>+•</sup> and arenes follow Rehm–Weller–Marcus kinetics and afford efficient preparation of arene<sup>+•</sup> cation radicals using visible light.

The properties of fullerene anionic and cationic radicals<sup>1</sup> are of much interest both from a theoretical standpoint and relative to their application in studies of electron-transfer dynamics<sup>2,3</sup> or as intermediates in the synthesis of fullerene derivatives.<sup>4</sup> The availability, stability, and broad visible absorption<sup>5</sup> of C<sub>60</sub>, as well as the high yield and long lifetime of its triplet,<sup>6</sup> facilitate its use as a light harvester and photosensitizer, acting as either energy- or electron-transfer agent.<sup>3b</sup> In this regard, the easy first reduction of C<sub>60</sub> (−0.44 V vs SCE in CH<sub>2</sub>Cl<sub>2</sub>),<sup>7</sup> together with the triplet energy<sup>8</sup>  $E_T = 1.56 \text{ eV}$ , permits the anion radical to be readily formed photochemically by direct electron transfer to the triplet from suitable donors.<sup>9</sup> In contrast, C<sub>60</sub><sup>+•</sup> ( $E^{\text{ox}} \approx 1.76 \text{ V vs SCE in benzonitrile}$ )<sup>10</sup> has thus far mainly been obtained by oxidation of the ground state either electrochemically<sup>10</sup> or photochemically using various sensitizers and cosensitizers<sup>4,11</sup> or by solvent radicals produced radiolytically.<sup>2,12</sup> More recently, the C<sub>60</sub><sup>+•</sup> cation radical has been prepared in solution by chemical oxidation of C<sub>60</sub> using as the oxidant a triarylamine cation radical coupled to a carborane anion.<sup>13</sup> Other methods have also been used, such as photoionization by argon resonance radiation in solid argon.<sup>14</sup>

Direct oxidation of fullerene triplets has been attempted using the powerful oxidants TCNQ and TCNE in nonpolar and polar solvents.<sup>15</sup> Both reagents quench the C<sub>60</sub> triplet, but a flash transient showing ion–radical absorption is only seen for TCNE in benzonitrile. On the basis of first-order decay, this is assigned to a CT complex, not to separated radicals.<sup>15a</sup>

Such photooxidations, whether of the ground state or of the triplet, are generally not very efficient, essentially because fast radical recombination competes with radical separation.<sup>16</sup> In this paper, we compare the effects of strongly acidic (TFA) and weakly acidic (HFIPA) H-bonding agents on the oxidation of <sup>3</sup>C<sub>60</sub> to C<sub>60</sub><sup>+•</sup> by chloranil. Although both additives increase the triplet quenching rate, we show that TFA gives slower back reactions and higher yields because of fast protonation of the

chloranil anion radical.<sup>17–19</sup> We also obtain the spectrum of C<sub>60</sub><sup>+•</sup> throughout the visible and near-IR regions, including its extinction coefficient at 980 nm, and study the kinetics of its charge-shift reactions with aromatic molecules.

## Experimental Section

Flash photolysis studies were carried out with a flashlamp-driven dye laser (Cyanosure ED-200) giving 0.2- $\mu\text{s}$  pulses at 590 nm (rhodamine 6G). Details of the apparatus and procedure have been described previously.<sup>3c</sup> C<sub>60</sub> (99.9%, from SES Research) was used without further purification to prepare  $\sim 10^{-4} \text{ M}$  solutions in CH<sub>2</sub>Cl<sub>2</sub>. Samples were purged with nitrogen. Chloranil (CA) and arenes (from Aldrich) were recrystallized. 4,4'-Dimethoxystilbene (DMS) was a generous gift from Dr. S. Farid of Eastman-Kodak Co. Methylene chloride was dried over molecular sieve 4A (Aldrich). Trifluoroacetic acid (TFA), 1,1,1,3,3,3-hexafluoro-2-propanol (HFIPA) and 2,2,2-trifluoroethanol (TFE) were >99% grade from Aldrich and were used as received. Hydrogen-bonding equilibrium constants between chloranil and additives (ROH) were determined by the Mataga method,<sup>20</sup> plotting  $(1 - A_0/A)/[\text{ROH}]$  vs  $A_0/A$ , where  $A_0$  and  $A$  are the quinone absorbances at a suitable wavelength without and with added ROH, respectively. The intercept of the plot is  $-K_{\text{HB}}$ .

For best accuracy in rate measurements, the concentrations of CA and H-bonding additives were mutually adjusted to obtain triplet lifetimes between 1 and 2  $\mu\text{s}$ , compared to about 40  $\mu\text{s}$  for the unquenched triplet. CA concentrations varied from  $4 \times 10^{-3}$  to  $3 \times 10^{-4} \text{ M}$  and HFIPA concentration from 0.1 to 0.7 M. The concentration of TFA was limited to <0.5 M because of chemical instability of the solution at higher concentrations.

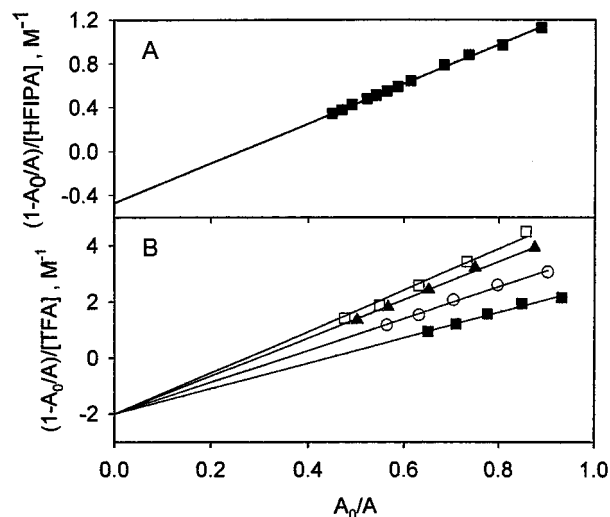
## Results and Discussion

**1. H-Bonding Equilibrium Constants.** Mataga plots,<sup>20</sup> using the small red shift in the  $\pi-\pi^*$  ( $S_2-S_0$ ) band of chloranil caused by H-bonding, were linear (Figure 1), and no indication was found for separate two-step bonding at the two quinone oxygens.

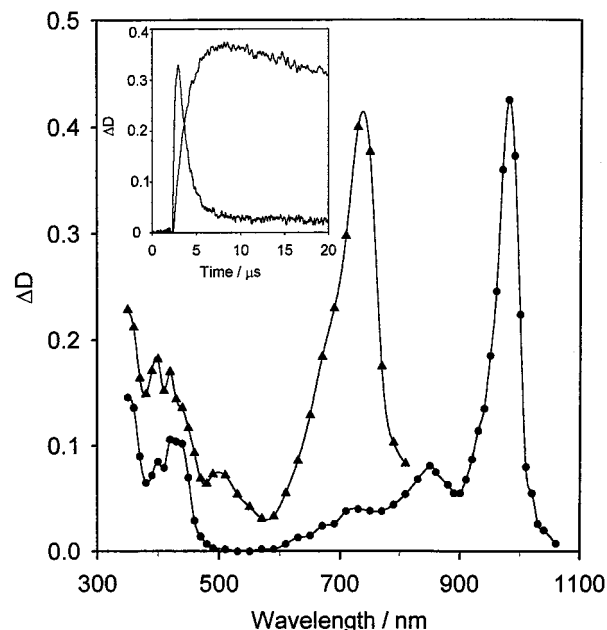
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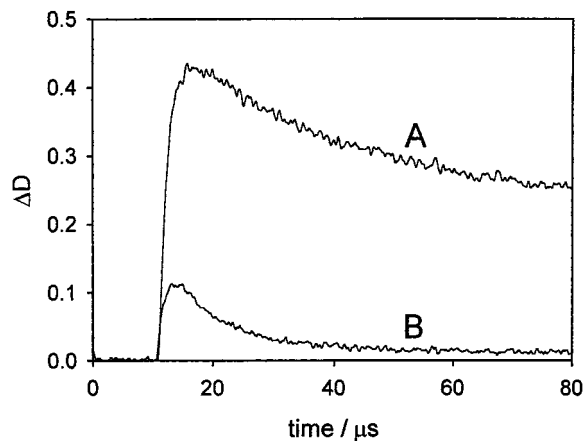
**Figure 1.** Determination of H-bonding equilibrium constants: (A) chloranil + HFIPA,  $\lambda = 310$  nm; (B) chloranil + TFA,  $\lambda$  (nm) = (□) 306, (▲) 308, (○) 310, and (■) 312.



**Figure 2.** Time-resolved absorption spectra in a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{C}_{60}$ , 0.3 mM chloranil, and 0.5 M TFA (▲) immediately and (●) 5.5  $\mu\text{s}$  after the laser flash. Inset: Triplet decay at 750 nm and growing-in of  $\text{C}_{60}^{+\bullet}$  cation radical absorption at 980 nm.

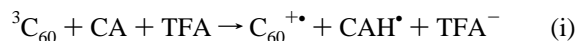
The  $K_{\text{HB}}$  values were  $2.0 \pm 0.2$  and  $0.5 \pm 0.1 \text{ M}^{-1}$  for bonding of CA to TFA and HFIPA, respectively. These H-bonding constants are quite close, compared to the very large difference in the proton acidities of the additives: the  $\text{p}K_{\text{a}}$  of TFA is 0.52, whereas that of HFIPA is 9.3.<sup>21</sup> In DMSO, the respective  $\text{p}K_{\text{a}}$ 's are 3.45 and 17.85.<sup>22,23</sup>

**2. Transient Absorption Spectra.** Figure 2 presents time-resolved spectra of a  $\text{C}_{60}$ -CA-0.5 M TFA solution, immediately and 5.5  $\mu\text{s}$  after laser excitation of the fullerene at 590 nm. The initial spectrum, with a peak at 750 nm and lesser bands around 500 and 400 nm, is that of triplet  $\text{C}_{60}$ .<sup>9b</sup> After the complete triplet decay, two bands are seen at 980 and 850 nm, which are unambiguously assigned to the cation radical,  $\text{C}_{60}^{+\bullet}$ , on the basis of general agreement with earlier spectroscopic results<sup>1,2,4,10a,11-13</sup> in the region 600–1000 nm, together with ESR measurements.<sup>10a</sup> The inset to Figure 2 shows that the 980-nm peak grows in at the same rate as triplet decay. The sharply



**Figure 3.** Back reaction following photooxidation of  $\text{C}_{60}$  by chloranil (CA) in  $\text{CH}_2\text{Cl}_2$ . Decay of  $\text{C}_{60}^{+\bullet}$  at 980 nm: (A)  $\text{C}_{60} + 0.3 \text{ mM CA} + 0.5 \text{ M TFA}$ , (B)  $\text{C}_{60} + 1.2 \text{ mM CA} + 0.7 \text{ M HFIPA}$ .

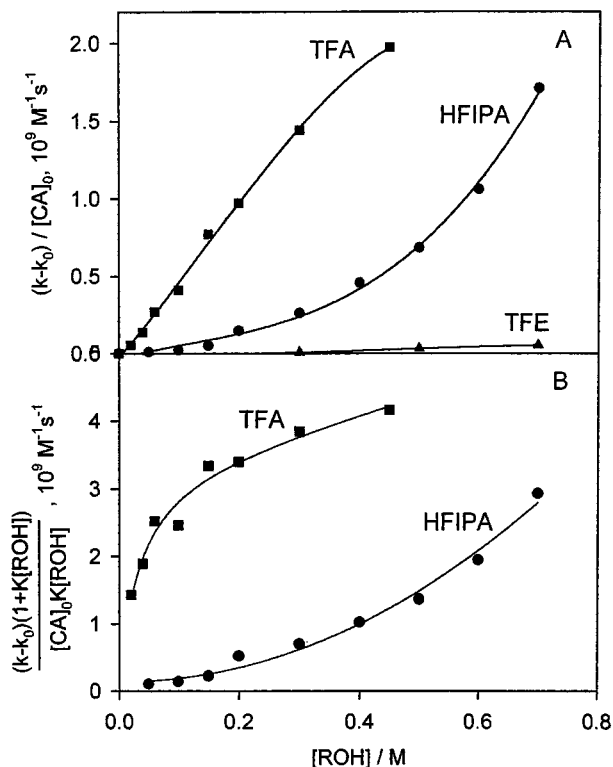
rising and well-defined peak at 430–435 nm corresponds to the spectrum of chloranil semiquinone,<sup>24</sup>  $\text{CAH}^{\bullet}$ , not to the anion radical  $\text{CA}^{\bullet-}$ , whose absorption is broad and lies slightly to the red.<sup>25</sup> Corrections to the spectra of Figure 2 due to bleaching of ground-state  $\text{C}_{60}$  are negligible, in view of the very low extinction coefficient of  $\text{C}_{60}$  throughout the visible region.<sup>5,6</sup> We thus establish the reaction



The transient spectrum obtained with HFIPA is similar to that of Figure 2, except that the heights of the peaks at 980 and around 440 nm are much diminished relative to those of the initial triplet (see below). In particular, the low intensity makes it uncertain whether the 440-nm band is due to  $\text{CAH}^{\bullet}$  or the close-lying  $\text{CA}^{\bullet-}$ . The question is resolved by the kinetics of the back reaction (Figure 3). The 980- and 440-nm transients in CA-HFIPA solution decay by fast second-order kinetics, corresponding to simple back electron transfer between oppositely charged radicals. However, in CA-TFA solutions, the radicals are much longer-lived, and their decay is not simply second-order. Here, the back reactions are not subject to restoring Coulomb forces but involve heavy-particle movement and might include dimerization of radicals as well.<sup>26</sup> We conclude that protonation of the  $\text{CA}^{\bullet-}$  radical anion occurs with TFA but not with HFIPA. This is consistent with the  $\text{p}K_{\text{a}}$  of  $\text{CA}^{\bullet-}$  ( $\sim 2$ ),<sup>27</sup> compared to 0.52 for TFA and 9.3 for HFIPA quoted above.

This conclusion is also in accord with the effects of H-bonding reagents on the electrochemistry of quinones. We have previously shown that the addition of TFA results in a positive shift in the chloranil reduction potential (assigned to the reduction of H-bonded, not protonated, chloranil) and causes the reduction to become irreversible, whereas these effects do not appear with HFIPA.<sup>17</sup> In the latter case, the cyclic polarogram is interpreted in terms of stabilization of reduction products by H-bonding.<sup>17</sup>

**3. Quenching of  ${}^3\text{C}_{60}$  by H-Bonded Chloranil.** Quenching of triplet  $\text{C}_{60}$  by chloranil is a slow process, with a rate constant of  $2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  in benzonitrile<sup>3b</sup> and a negligible rate in less-polar  $\text{CH}_2\text{Cl}_2$ . The addition of H-bonding reagents, ROH, enhances the rate. The experimental quenching rate data, measured at the 750-nm triplet peak, are compactly summarized in Figure 4A, where the observed pseudo-first-order rate enhancement,  $k - k_0$ , normalized with respect to the total CA concentration,  $[\text{CA}]_0$ , is plotted against the TFA, HFIPA, and



**Figure 4.** Quenching of <sup>3</sup>C<sub>60</sub> by chloranil and H-bonding agents (ROH). (A) Pseudo-first-order rate constants referred to total chloranil concentration [CA]<sub>0</sub> vs [ROH]. (B) Quenching rate constants for H-bonded CA vs [ROH].

TFE concentrations. TFE has very little effect on the rate compared to TFA and HFIPA.

Figure 4B shows rate constants,  $k_q$ , calculated assuming that quenching is due to H-bonded chloranil, CA<sub>HB</sub>, with equilibrium constant  $K$

$$k - k_0 = k_q[CA_{HB}]$$

$$k_q = \frac{(k - k_0)(1 + K[ROH])}{K[CA]_0[ROH]} \quad (1)$$

It is evident that these rate constants depend on the TFA or HFIPA concentrations. The TFA enhanced rate rises about 3-fold over the concentration range 0.02–0.3 M and then increases more slowly as the rate approaches diffusion control. A much stronger dependence is found for HFIPA, where the rate rises, with increasing slope, about 30-fold from 0.05 to 0.7 M.

The linear Mataga plots (Figure 1) indicate that the H-bonding of CA in these cases follows 1:1 stoichiometry (eq 1) and clearly cannot account for the rising profile of the HFIPA curve in Figure 4. However, these agents can bond to each other as well as to quinone and can be expected to do so in CH<sub>2</sub>Cl<sub>2</sub> solution. Thus, we attribute the [ROH] dependence in Figure 4 to local clusters of H-bonding molecules surrounding the chloranil and favoring coupled proton transfer to CA<sup>-•</sup> by TFA or stabilization of charged products by solvation or H-bonding with HFIPA. Indeed, in the electrochemical studies cited previously, we have estimated the size of such clusters from shifts in quinone reduction potentials caused by H-bonding agents.<sup>17</sup> In the TFA curve of Figure 4, the smaller relative change of rate with concentration can be understood in view of the very low pK<sub>a</sub>, which favors fast proton transfer even in the absence of a large cluster. The negligible effect of TFE might relate to its much

**TABLE 1: Rate Constants for the Oxidation of Aromatic Compounds with C<sub>60</sub><sup>+•</sup> Cation Radical in CH<sub>2</sub>Cl<sub>2</sub> Solution Containing 0.5 M TFA and Their Oxidation Potentials**

aromatic compound	$k_{et}$ (10 <sup>8</sup> M <sup>-1</sup> s <sup>-1</sup> )	$E^{ox}$ (V vs SCE)	$-\Delta G^d$ (eV)
1 anthracene	47.	1.09 <sup>a</sup>	0.67
2 pyrene	60.	1.16 <sup>a</sup>	0.60
3 2,3-dimethylnaphthalene	52.	1.38 <sup>a</sup>	0.38
4 hexamethylbenzene	46.	1.52 <sup>b</sup>	0.24
5 2-methoxynaphthalene	46.	1.52 <sup>a</sup>	0.24
6 fluoranthene	4.9	1.64 <sup>b</sup>	0.12
7 phenanthrene	2.3	1.68 <sup>b</sup>	0.08
8 naphthalene	0.36	1.72 <sup>b</sup>	0.04
9 mesitylene	0.005	1.80 <sup>c</sup>	-0.04
10 biphenyl	<0.001	1.91 <sup>b</sup>	-0.15

<sup>a</sup> In acetonitrile. Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993. <sup>b</sup> In acetic acid. Ebersson, L.; Nyberg, K. *J. Am. Chem. Soc.* **1966**, *88*, 1686. <sup>c</sup> In acetonitrile. Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124. <sup>d</sup> Referred to  $E^{ox}(C_{60}) = 1.76$  V vs SCE.<sup>10</sup>

smaller H-bonding power compared to that of HFIPA.<sup>17,21</sup> Finally, we note that the concave form of the HFIPA function in Figure 4 is very similar to the form of rate vs additive curves in the reductive quenching of <sup>3</sup>C<sub>60</sub> by phenols in nonpolar solvents in which pyridines are the H-bonding additives.<sup>28</sup> These observations have also been interpreted in terms of local solvation, which favors electron transfer even without coupled proton transfer.<sup>28</sup>

**4. Determination of Radical Yields.** Yields in reaction i were determined by using a charge-shift reaction to convert C<sub>60</sub><sup>+•</sup> to a second cation radical, M<sup>+•</sup>, whose molar extinction coefficient is precisely known

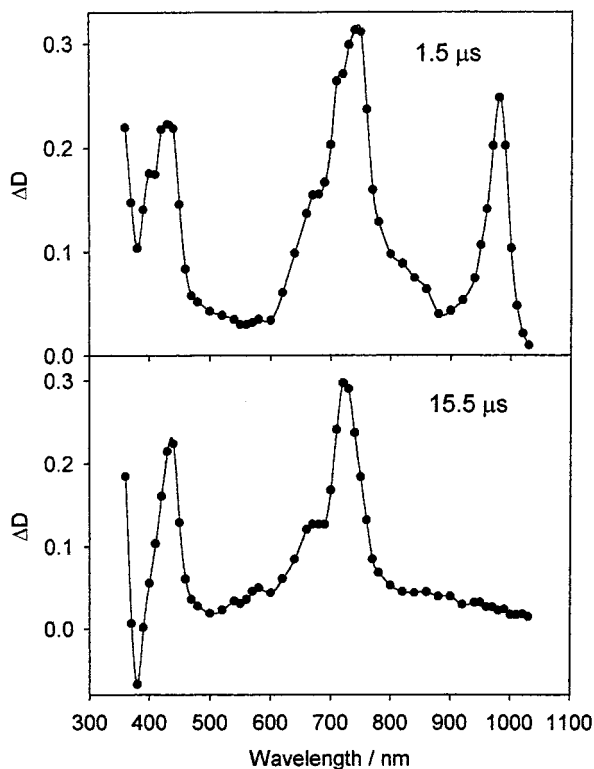


Anthracene and pyrene were chosen as donors because they reduce C<sub>60</sub><sup>+•</sup> at diffusion-controlled rates, corresponding to their low oxidation potentials relative to that of C<sub>60</sub> (Table 1). This permits almost quantitative trapping of C<sub>60</sub><sup>+•</sup> at such low concentrations that secondary reactions of M<sup>+•</sup>, such as M<sub>2</sub><sup>+•</sup> formation, do not interfere.<sup>29</sup> The charge-shift reaction is demonstrated in Figure 5, which shows transient absorption spectra in a C<sub>60</sub>–CA–0.5 M TFA solution containing anthracene (An) as the electron donor. The spectrum at 1.5 μs after laser excitation is a composite of residual absorption of <sup>3</sup>C<sub>60</sub> at 750 nm, C<sub>60</sub><sup>+•</sup> at 980 nm, and shoulders at 720 and 680 nm due to developing An<sup>+•</sup>. The band in the 400–450-nm region originates from closely overlapping absorption of chloranil semiquinone and An<sup>+•</sup>.<sup>29,30</sup> At 15.5 μs after flashing, C<sub>60</sub><sup>+•</sup> is completely reduced, and the spectrum above 450 nm, with a peak at 720 nm and no interference from other bands in this region, agrees well with earlier measurements of An<sup>+•</sup>.<sup>29,30</sup> The peak at 435 nm is higher than expected for An<sup>+•</sup> alone, because of the contribution of the semiquinone. The An<sup>+•</sup> radical is rather long-lived under these conditions (>1 ms) and decays by a second-order process.

The yield of C<sub>60</sub><sup>+•</sup> is then obtained from eq 2

$$\Phi_R = \frac{\Delta D^0(M^{+•}) \epsilon(C_{60})}{\Delta D^0(C_{60}) \epsilon(M^{+•})} \quad (2)$$

where the absorbance changes are measured at the same laser energy and  $\Delta D^0(M^{+•})$  is the value of the M<sup>+•</sup> absorbance corrected for any decay during the growing-in period.<sup>31</sup> Measurements were made on CH<sub>2</sub>Cl<sub>2</sub> solutions containing  $3 \times 10^{-4}$



**Figure 5.** Charge-shift reaction in  $\text{CH}_2\text{Cl}_2$ :  $\text{C}_{60} + 0.3 \text{ mM chloranil} + 0.5 \text{ M TFA} + 0.1 \text{ mM anthracene}$ .  $\text{C}_{60}^{+\bullet} + \text{An} \rightarrow \text{C}_{60} + \text{An}^{+\bullet}$ .

M CA and 0.5 M TFA, in which  $10^{-4}$  M An trapped over 97% of  $\text{C}_{60}^{+\bullet}$ . From our earlier work, we take  $\epsilon(^3\text{C}_{60}) = 16\,100 \text{ M}^{-1} \text{ cm}^{-1}$  at 750 nm,<sup>9b</sup> which agrees precisely with the value determined by Ebbesen et al.<sup>32</sup> and leads to  $^3\text{C}_{60}$  yields close to unity, as found by other methods.<sup>6</sup> With  $\epsilon(\text{An}^{+\bullet}) = 11\,600 \text{ M}^{-1} \text{ cm}^{-1}$  at 720 nm,<sup>33</sup> the average of several experiments gave  $\Phi_{\text{R}} = 0.81 \pm 0.08$  for the yield of  $\text{C}_{60}^{+\bullet}$  in reaction i.

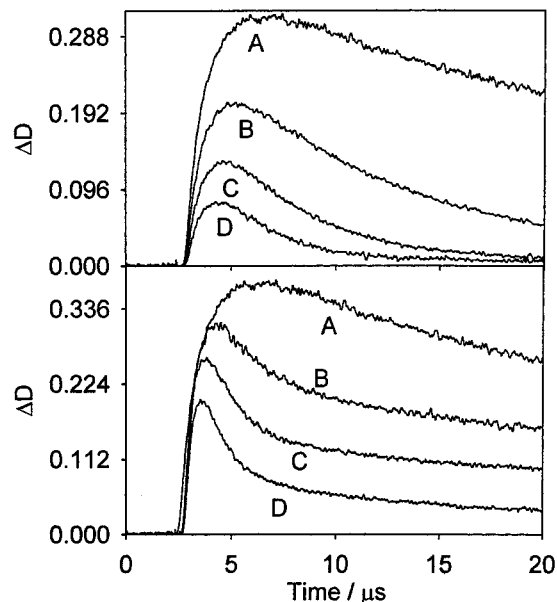
Independent measurements using pyrene as the donor [ $\epsilon(\text{pyrene}^{+\bullet}) = 48\,000 \text{ M}^{-1} \text{ cm}^{-1}$  at 450 nm<sup>34</sup>] gave  $\Phi_{\text{R}} = 0.73 \pm 0.08$ , in fair agreement with the result obtained with anthracene. Averaging these values, we take  $\Phi_{\text{R}} = 0.77$  in further calculations.

Lower yields with HFIPA-induced quenching were measured using 4,4'-dimethoxystilbene (DMS) as the donor to  $\text{C}_{60}^{+\bullet}$ . The  $\text{DMS}^{+\bullet}$  radical absorbs at 530 nm where there are no overlapping transient bands in the flash spectra and also offers the usefully high extinction value<sup>35</sup>  $\epsilon(\text{DMS}^{+\bullet}) = 65\,600 \text{ M}^{-1} \text{ cm}^{-1}$ . The rate constant for the charge shift  $\text{C}_{60}^{+\bullet} \rightarrow \text{DMS}^{+\bullet}$  at  $[\text{HFIPA}] = 0.7 \text{ M}$  was  $4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , and the  $\text{C}_{60}^{+\bullet}$  yield was 0.15.

**5. Determination of  $\text{C}_{60}^{+\bullet}$  Extinction Coefficient: The Spectrum of  $\text{C}_{60}^{+\bullet}$ .** Despite the many studies of the  $\text{C}_{60}^{+\bullet}$  spectrum, a value for the extinction coefficient has been given only very recently by Webster and Heath.<sup>10a</sup> With the measured  $\Phi_{\text{R}}$  values, we obtain  $\epsilon(\text{C}_{60}^{+\bullet})$  from the ratio of  $\text{C}_{60}^{+\bullet}$  absorbance at 980 nm and the initial absorbance of the triplet at 750 nm

$$\begin{aligned} \epsilon^{980}(\text{C}_{60}^{+\bullet}) &= \frac{\Delta D^0(\text{C}_{60}^{+\bullet})}{\Delta D^0(\text{M}^{+\bullet})} \epsilon(\text{M}^{+\bullet}) \\ &= \frac{\Delta D^0(\text{C}_{60}^{+\bullet})}{\Delta D^0(^3\text{C}_{60})} \frac{\epsilon^{750}(^3\text{C}_{60})}{\Phi_{\text{R}}} \end{aligned} \quad (3)$$

The values of  $\epsilon(\text{C}_{60}^{+\bullet})$  at 980 nm thus obtained were  $25\,500 \pm 2500 \text{ M}^{-1} \text{ cm}^{-1}$  taking  $\Phi_{\text{R}} = 0.77$  in 0.5 M TFA and  $24\,700 \pm$

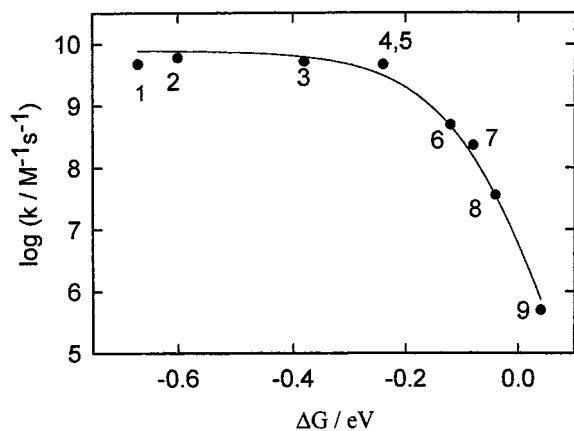


**Figure 6.** Charge-shift kinetics and formation of cation radical dimer:  $\text{C}_{60} + 0.6 \text{ mM chloranil} + 0.5 \text{ M TFA}$  in  $\text{CH}_2\text{Cl}_2$ . Transient absorption profiles at 980 nm. Upper panel: With added 1,3,5-trimethylbenzene at concentrations of (A) 0.02, (B) 0.18, (C) 0.36, and (D) 0.54 M. Lower panel: With added 2,3-dimethylnaphthalene at concentrations of (A) 0, (B) 0.05, (C) 0.1, and (D) 0.15 mM.

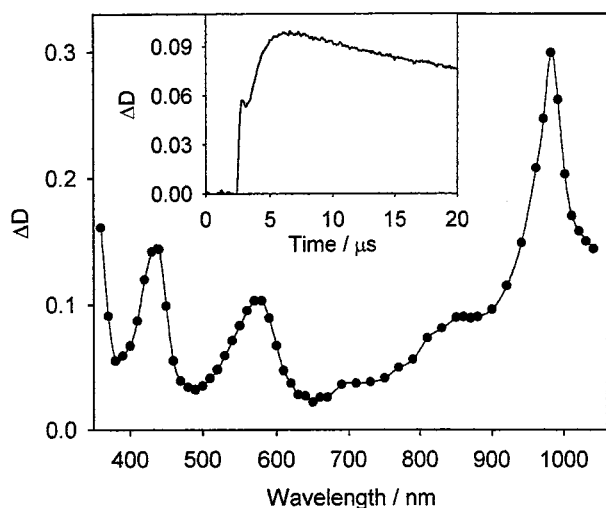
$2500 \text{ M}^{-1} \text{ cm}^{-1}$  taking  $\Phi_{\text{R}} = 0.15$  at 0.7 M HFIPA. These closely agreeing results are much higher than the recent value,  $\epsilon(\text{C}_{60}^{+\bullet}) = 11\,000 \text{ M}^{-1} \text{ cm}^{-1}$  in 1,1',2,2'-tetrachloroethane, derived from careful spectro-electrochemical measurements.<sup>10a</sup> In this regard, some general comment on the spectrum of  $\text{C}_{60}^{+\bullet}$  is warranted.

Figure 2 shows that the absorption of  $\text{C}_{60}^{+\bullet}$  is remarkably low in the region 500–600 nm and that this window might even extend down to 400 nm. Such a broad, low-absorbing region is also predicted by CNDO/S calculations.<sup>12</sup> In agreement with this finding, the ratio  $\Delta D(435 \text{ nm})/\Delta D(980 \text{ nm}) = 0.24$ , measured directly from the peaks of Figure 2, is reasonably close to the corresponding ratio of extinction coefficients,  $\epsilon^{435}(\text{CAH}^{+\bullet})/\epsilon^{980}(\text{C}_{60}^{+\bullet}) = 7700/25\,000 = 0.31$ , which assumes no overlapping  $\text{C}_{60}^{+\bullet}$  absorption at 435 nm and equivalent yields of the radicals. The spectrum of the fullerenium salt of Reed and Bolskar<sup>1</sup> similarly shows low absorption between 700 and about 450 nm but somewhat greater absorption around 500 nm than is indicated in Figure 2. However, the electrochemically generated spectrum shows substantial absorption at 550 nm, increasing steadily toward shorter wavelengths.<sup>10a</sup> Similar high absorption below 500 nm was found by Kato et al.<sup>12</sup> Such spectra suggest the presence of species such as  $\text{HC}_{60}^{+\bullet}$  or  $\text{RC}_{60}^{+\bullet}$  that do not absorb in the near-IR region,<sup>13</sup> and whose formation might account for the low extinction coefficient of  $\text{C}_{60}^{+\bullet}$  given by Webster and Heath. The band at 650 nm observed in the radiolytic study by Hou et al.<sup>36</sup> is probably due to such species, not to  $\text{C}_{60}^{+\bullet}$ .

**6. Production of Aromatic Cation Radicals.** The production of aryl cation radicals by oxidation with  $\text{C}_{60}^{+\bullet}$ , as seen above for An and Py, occurs also with many other arenes and offers an efficient photochemical pathway to these radicals using visible light. As a representative example, Figure 6 shows the decay of  $\text{C}_{60}^{+\bullet}$  absorption at 980 nm caused by increasing concentrations of 1,3,5-trimethylbenzene (TMB). Pseudo-first-order decay rates derived from these curves are linear in the concentration of TMB, and the slope gives the electron-transfer rate constant. Table 1 summarizes these constants for several



**Figure 7.** Logarithm of rate constant for the electron transfer between C<sub>60</sub><sup>++</sup> and arenes vs reaction free energy (Table 1).



**Figure 8.** Formation of (naphthalene)<sub>2</sub><sup>++</sup> dimeric cation radical: transient absorption spectrum in CH<sub>2</sub>Cl<sub>2</sub> with C<sub>60</sub>, 0.6 mM chloranil, 0.5 M TFA, and 14 mM naphthalene, 4 μs after flash. Inset: Transient absorption at 560 nm.

arenes and lists their oxidation potentials vs SCE. In conjunction with  $E^{\text{ox}}(\text{C}_{60}) = 1.76$  V vs SCE in benzonitrile,<sup>10</sup> we obtain  $\Delta G^\circ$  for electron transfer from arene to C<sub>60</sub><sup>++</sup>. The logarithms of these rate constants are plotted against  $\Delta G^\circ$  in Figure 7. At  $\Delta G^\circ = 0$ , the slope of the plot corresponds closely to the limiting Rehm–Weller–Marcus slope,<sup>37</sup>  $(2.3RT)^{-1} = -16.9$  eV<sup>-1</sup>. At higher driving force, the rate rises and levels off at the diffusion-controlled limit. The Marcus inverted region is not accessible in these systems because compounds with oxidation potentials lower than that of anthracene are not stable in strongly oxidizing CA + 0.5 M TFA solutions. Moreover, such compounds can reduce <sup>3</sup>C<sub>60</sub><sup>3a</sup> or undergo energy transfer, as we have shown for perylene and tetracene<sup>3b</sup>. In related work, Guldi and Asmus have studied the oxidation of C<sub>76</sub> and C<sub>78</sub> by arene<sup>++</sup> cation radicals,<sup>2a</sup> which is the reverse of the reaction discussed here, and find indications of an inverted region at  $\Delta G^\circ < -0.8$  eV.

In several cases of arene oxidation by C<sub>60</sub><sup>++</sup>, long-lived absorption persists following transient decay at 980 nm, as shown in Figure 6 for 2,3-dimethylnaphthalene. We attribute this phenomenon to arene dimer cation radicals, M<sub>2</sub><sup>++</sup>, which usually absorb strongly in the near-IR region.<sup>38</sup> Such dimer formation will occur with arenes, which react at slower-than-diffusion-controlled rates and which require relatively high concentrations for efficient reduction of C<sub>60</sub><sup>++</sup>. We observed dimer formation for several arenes using absorption bands in

the visible region. Figure 8 shows the transient spectrum at 4 μs after laser excitation of a C<sub>60</sub> solution containing 0.6 mM CA, 0.5 M TFA, and 15 mM naphthalene. In addition to the semiquinone and C<sub>60</sub><sup>++</sup> bands at 435 and 980 nm, respectively, a new band appears at 560 nm, which corresponds to the (naphthalene)<sub>2</sub><sup>++</sup> dimer radical<sup>39</sup> (naph)<sub>2</sub><sup>++</sup>. The inset (Figure 8) shows the growing-in of this absorption following the flash. Pulse radiolysis measurements showed<sup>39</sup> that the equilibrium constant for (naph)<sub>2</sub><sup>++</sup> formation in benzonitrile is 520 M<sup>-1</sup>, and the dimerization rate constant (in acetone at 258 K) is<sup>40</sup>  $6.32 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. As this rate is 2 orders of magnitude higher than the electron-transfer rate from naphthalene to C<sub>60</sub><sup>++</sup> ( $k = 6.8 \times 10^7$  M<sup>-1</sup> s<sup>-1</sup>), only the dimer cation radical, which absorbs in both the visible and near-IR regions, can be detected.

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