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The Spike in the $C_{60}^{\bullet -}$ ESR Spectrum: Oxygen Effect and Negative Temperature Dependence of the $C_{60}O_2^{\bullet -}$ Isomerization Rate

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A stable, broad ESR signal ($g = 1.998$, $\Delta H_{pp} = 37.0$ G) of the $C_{60}^{\bullet -}$ anion radical was generated by irradiation of a C_{60}−toluene solution in the presence of organic salt, $[(ph)_3P]_2N^+(ph)^4B^-$, and 14.3% methanol. Upon exposure to molecular oxygen, the broad band gradually diminishes and a narrow band of $g = 2.0008$ and $\Delta H_{pp} = 3.32$ G (hereafter, band b) grows, which further transforms to another narrow band of $g = 2.0026$ and $\Delta H_{pp} = 1.67$ G (hereafter, band c). The transformation rate of bands b to c was found to be negative temperature dependent, i.e., the higher the temperature, the slower the transformation rate. At high temperatures (e.g., 365 K) and in polar solvents (e.g., 30% methanol in toluene), band c can reversibly transform back to band b. Microwave power saturation experiments show that band c has much longer relaxation times than band b. Both bands b and c resemble the "spike" commonly observed in the $C_{60}^{\bullet -}$ anion radical ESR spectra and were designated to two isomers of the $C_{60}O_2^{\bullet -}$ anion radical. A kinetic model was derived to account for the negative temperature-dependent transformation rate of bands b to c.

Introduction

The discovery[1] of fullerenes has initiated a great deal of interest in the basic properties[2,3] and potential applications[4] of this new form of carbon allotrope. Upon doping of 3 equiv of strong reducing metals, M_xC_{60} (M = Na, K, Rb, Cs, etc.) becomes a superconductor with $T_c \leq 40$ K.[5] It is often wondered whether C_{60} is a truly three-dimensional superaromatic molecule, and whether electrons can delocalize among the whole fullerene cage.[6] Theoretical calculation[7] and experimental observations[8] show that there exist ring currents on the fullerene cage. In radical addition studies, however, it was found that the radical tends to localize at the carbon immediately adjacent to the substituent group.[9] On the other hand, ESR studies show that ^{13}C hyperfine coupling to the triplet state of C_{60} signal is unusually small.[10] It was shown that Jahn−Teller distortion of the triplet degenerated LUMO obitals of C_{60} plays an important role to the structure[11] and ESR patterns[12] of triplet C_{60} and $C_{60}^{\bullet -}$ anion radicals. Currently, it is still under debate whether the C_{60}^{2-} dianion radical is paramagnetic or diamagnetic.[13,14]

In the ESR studies of $C_{60}^{\bullet -}$, C_{60}^{2-}, and C_{60}^{3-} anion radicals, it is always observed that a sharp "spike" exists on top of the broad $C_{60}^{\bullet n-}$ ($n = 1$, 2, and 3) band.[13−18] The identity of this spike is unclear. It not only puzzles many laboratories but also affects the correct assignment and therefore the properties of the $C_{60}^{\bullet n-}$ anion radicals. Greaney and Gorun[15] assigned the spike and the broad band to be free and ion paired $C_{60}^{\bullet -}$, respectively. Kadish and co-workers[16] designated the spike to be C_{60}^{2-}, which was formed via disproportionation of two $C_{60}^{\bullet -}$. Reed and co-workers[12a] proposed that the spike arises from thermal population of a low-lying excited state of $C_{60}^{\bullet -}$. From experimental observations that the spike is readily saturated by microwave, and has nearly unchanged line width within 5−300 K, Eaton and co-workers[13b,17] rationalized that the spike has to be from substituted C_{60} derivatives with lower symmetry and higher barrier to molecular rotation than C_{60}. Moriyama et al.[18] observed that the spike is actually composed of two bands (B_2 and B_1), and assigned B_2 and B_1 as a loosely ion paired and free $C_{60}^{\bullet -}$, respectively.

In this study, we observed that upon exposure to molecular oxygen, the broad $C_{60}^{\bullet -}$ band was slowly converted to a narrow band (i.e., the band b) with $g = 2.0008$ and $\Delta H_{pp} = 3.32$ G. This band b then further transforms to another narrow band (i.e., the band c) with $g = 2.0026$ and $\Delta H_{pp} = 1.67$ G. This transformation rate was found to be inverse temperature dependent, i.e., slower transformation rates at higher temperatures. At high temperatures ($T > 355$ K) and in polar environment (30% methanol in toluene), the band c can be reversibly converted back to the band b. Both bands b and c resemble the spike(s) commonly observed in literature and were assigned to two isomers of the $C_{60}O_2^{\bullet -}$ anion radical.

Experimental Section

Substrates and solvents used in this study are as follows: C_{60} (99.9%, MER, Arizona), toluene (Aldrich, spectroscopic grade). Typically, 1.7 mM C_{60}−organic salt−toluene solution was prepared immediately before experiments. The organic salts, $[(ph)_3P]_2N^{\bullet +}(ph)_4B^-$, was synthesized by slowly mixing clear aqueous solution of $[(ph)_3P]_2N\cdot Cl$ (Aldrich) and of $Na\cdot(ph)_4B$ (Aldrich) together. The white $[(ph)_3P]_2N^+(ph)_4B^-$ precipitate was then recrystallized in ethanol twice. Another organic salt, $(ph)_4P^+(ph)_4B^-$, was also recrystallized in ethanol twice. The amount of an organic salt added is usually ∼1.0 mg/mL, where part of the organic salt exists as suspended particles. The percentage of methanol in the toluene solution is in the range of 14−30%, which quenches the $C_{60}^{\bullet +}$ cation radical and changes the solvent polarity. When 30% (v/v) of methanol was added to the C_{60}−organic salt−toluene solution, the two solvents first exist as two layers, then become miscible after a few seconds of sonication. The sample solution was deoxygenated via several freeze−pump−thaw cycles. At the final cycle, 1 atm of N_2 gas was usually filled into the JY-ESR tube. The deoxygenated solution was then irradiated by the output of a 500 W high-pressure Hg lamp via a water filter for 10−30 min. And all spectra were taken in the dark on a Bruker EMX-12 ESR spectrometer. A DPPH sample in a second resonator chamber was used as a reference for g value measurements. The temperature is controlled by a Bruker B-VT 2000 variable temperature control unit. The ESR parameters are listed in the

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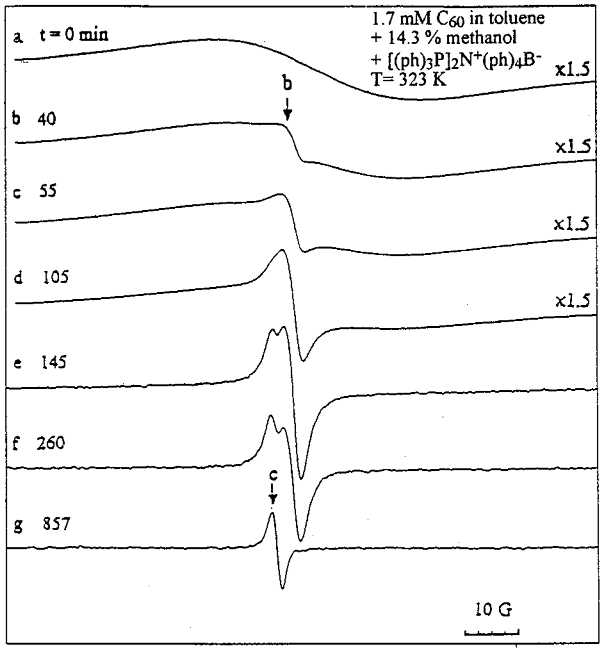


Figure 1. Irradiation of 1.7 mM C_{60} in methanol (14.3%)–toluene solution in the presence of an organic salt, $[(ph)_3P]_2N^+(ph)_4B^-$ (1 mg/mL) generates the spectrum in (a). Upon exposure to air at 323 K, the broad band spectrum in (a) gradually transforms to narrow bands b and c (spectra b to g, see the text for details). The exposure time is labeled on the figure. All spectra were taken in the dark. The ESR parameters are as follows: modulation 1.5 G, microwave power 20 dB, and scanning range 100 G.

figure captions. The magnitude of modulation is usually set to be smaller than the line width(s) of the signal(s) being observed.

Results

Previously, photoexcited triplet C_{60} was shown to undergo disproportionation and generate $C_{60}^{\bullet+}$ cation and $C_{60}^{\bullet-}$ anion radicals.[19] In the presence of an organic salt (such as $(ph)_4P^+(ph)_4B^-$, or $[(ph)_3P]_2N^+$ $(ph)_4B^-$), both $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ can be stabilized and observed by steady-state ESR measurements even after the light is off. The $C_{60}^{\bullet+}$ cation radical band ($g = 2.0016$, and $\Delta H_{pp} = 2.3$ G at 300 K) can be quenched by the presence of 6% methanol or 12% benzonitrile in toluene.[19,20] The broad $C_{60}^{\bullet-}$ band ($g = 1.998$, and $\Delta H_{pp} = 37$ G at 300 K) in Figure 1 was obtained by irradiation of 1.7 mM C_{60}–toluene solution in the presence of 14.3% methanol and the organic salt, $[(ph)_3P]_2N^+(ph)_4B^{\bullet-}$ Upon exposure of the solution to air, the broad $C_{60}^{\bullet-}$ band was slowly quenched, and a narrow band of $g = 2.0008$ and $\Delta H_{pp} = 3.32$ G (i.e., band b) simultaneously grew in within 2 h at 323 K (see Figure 1a–d). If pure molecular oxygen, instead of air, was used, the conversion rate becomes much faster (complete quenching within 30 min). If the sample was shaken in the presence of air, the conversion rate can also be speeded up. To examine whether the quenching by oxygen is reversible, the solution was reevacuated via several freeze–pump–thaw cycles. The peak height of band b remains unchanged.[21] Therefore, the quenching of $C_{60}^{\bullet-}$ by oxygen is via chemical bonding. By fitting the rise of band b (data not shown) to the function of $(1 - e^{-kt})$, one obtains an apparent oxygen quenching rate of 0.3×10^{-3} s^{-1}. The observed rate is the sum of rates of two processes, namely, solubilization of gaseous oxygen into the solution and chemical bonding of solubilized oxygen to the C_{60} cage. If the latter process is the rate-determining step, the observed rate will be increased by a factor of 5 by changing air to pure molecular oxygen, which seems consistent with experimental observation. However, by assuming an oxygen concentration of 1 mM in toluene, an intrinsic quenching rate of 0.3 M^{-1} s^{-1} was obtained, which is 5–9 orders of magnitude slower than the reported oxygen quenching rates of carbon center radicals in literature.[22] Therefore, it is more likely that the measured rate is the diffusion rate of gaseous oxygen into the C_{60}–toluene solution. Upon standing in the absence of oxygen, band b further transforms to another narrow band of $g = 2.0026$ and $\Delta H_{pp} = 1.67$ G (i.e., band c, see Figure 1d–g) within 12 h at 323 K.[23] The final intensity (double integrated area) of band c is smaller than the initial intensity (area) of band b. Two possible reasons are responsible for the small band c, i.e., longer relaxation times of band c than those of band b (see results below), and conversion of part of band b to other (diamagnetic) products. The species responsible for band c is very likely to be a geometric isomer of that responsible for band b. In other words, the species b is a kinetic product which then transforms itself into a thermally more stable conformation and generates species c (and therefore band c, vide infra). By fitting the decay of the band b to a single-exponential function, a transformation rate of 2.2×10^{-4} s^{-1} was obtained (see Figure 2).

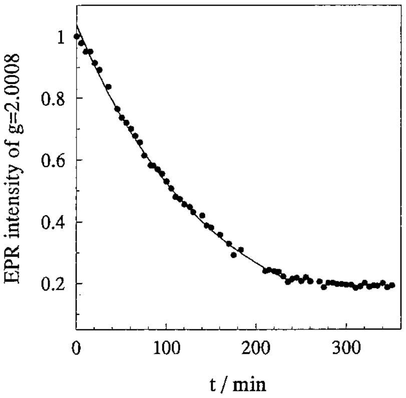


Figure 2. Decay of the ESR intensity of the band b at 328 K. The solid line is an exponential function of e^{-kt}, where $k = 2.2 \times 10^{-4}$ s^{-1}. The parameters of the ESR spectrometer are as follows: modulation 2.0 G, microwave power 20 dB, gain 5.0×10^5, and scan width 100 G.

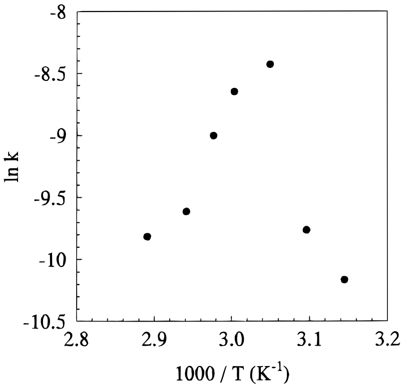


Figure 3. Natural logarithm of the transformation rate of bands b to c as a function of the reciprocal of temperature. The ESR signal is generated by irradiation of a sample of 1.7 mM C_{60} in methanol (14.3%)–toluene solution in the presence of $[(ph)_3P]_2N^+(ph)_4B^-$ (1 mg/mL), followed by exposure to air.

The transformation rate of bands b to c, to our surprise, increases to reach a maximum at $T \approx 328$ K, then continuously decreases at higher temperatures. The Arrhenius plot of ln(k) vs 1/T shows a curve-up shape with positive slopes (i.e., negative E_a values, see Figure 3) as $T > 328$ K. In the literature, the "negative activation energy" was observed in the reactions of radicals with neutral molecules,[24–26] radical recombination,[27]

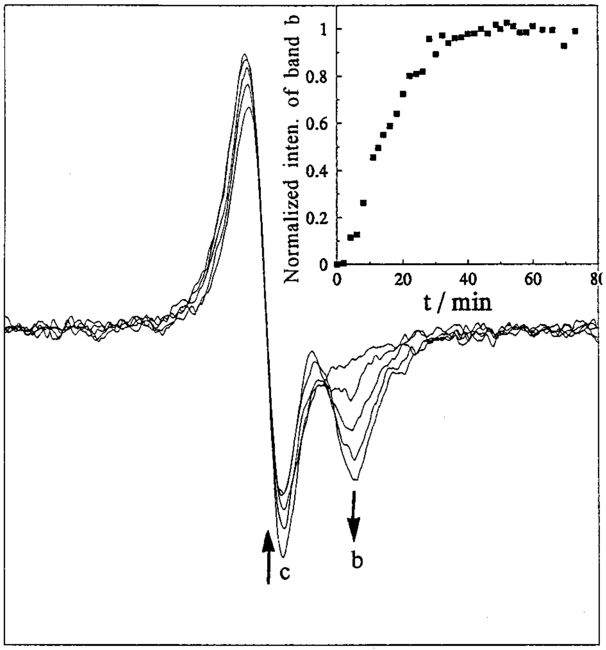


Figure 4. Reverse transformation of bands c to b upon temperature changes from 350 to 365 K. The solution is 1.4 mM C_{60} in toluene in the presence of 30% methanol and $[(ph)_3P]_2N^+(ph)_4B^-$ (1.0 mg/mL). The ESR parameters are as follows: modulation 2.0 G, microwave power 20 dB, gain 3.2×10^5, and scan width 100 G. The inset shows the normalized intensity of band b as a function of time.

decay of triplet biradicals,[28] a proton-transfer reaction,[29] DNA triplet formation,[30] and termolecular reactions.[31] These observations were commonly fit to the following model

$$R \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} P \qquad (I)$$

where the reactant R is in preequilibrium with an intermediate I. For a truly single-step reaction, the reaction rate will never be negative temperature dependent since the activation energy barrier is always positive. The term "negative activation energy" sometimes used in the literature is misleading and should be avoided. The negative temperature dependence of an observed reaction rate is a result of combination of several reaction steps. In the current system, species b might also equilibrate with an intermediate which then further transforms to species c.

In polar environment and at high temperatures (e.g., 30% methanol in toluene and 365 K), band c was reversibly converted back to band b to reach a final equilibrium b/c ratio of ~0.65 (measured at microwave power of 30 dB) within 50 min[32] (see Figure 4). Since the thermal equilibrium time (within 2 min from 350 to 365 K) is much shorter than the transformation time (~50 min), the system was considered to be under a "temperature jump" condition.[33] The decay of band c was therefore fit to an $e^{-(k_f+k_r)t}$ function (see inset of Figure 4). Together with the equilibrium constant K ($=k_f/k_r$), the transformation rates of bands b to c (k_f) and c to b (k_r) were deduced to be 8.26×10^{-4} and 5.37×10^{-4} s^{-1} at 365 K, respectively. The reversion of bands c to b was only observed in highly polar solvent and at high temperatures, indicating that species b is stabilized by polar environments and species c is favored in nonpolar environments.

The line widths of the $C_{60}^{\bullet-}[(ph)_3P]_2N^+$ complex, species b and c were measured as a function of temperature (see Figure 5). The line width of the $C_{60}^{\bullet-}[(ph)_3P]_2N^+$ complex decreases continuously from 38.0 G at 320 K to 20.0 G at 120 K. The low-temperature line width narrowing pattern of the $C_{60}^{\bullet-}$ anion radical is the same as those reported in the literature,[16a] while the line widths of bands b and c are very weakly temperature dependent. The line width of band b changes from 3.83 G at 347 K to 3.35 G at 136 K, whereas the line width of band c changes from 1.99 G at 360 K to 2.30 G at 118 K.

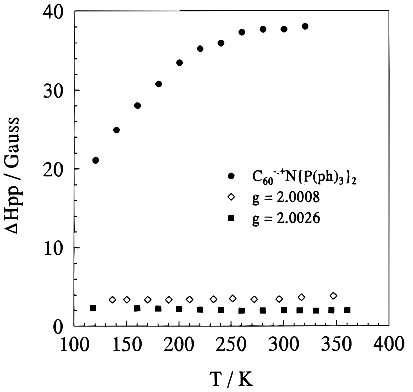


Figure 5. Line widths of the broad band $C_{60}^{\bullet-}$ anion radical, bands b and c, as a function of temperature. The microwave power is 20 dB and modulation 1.5 G.

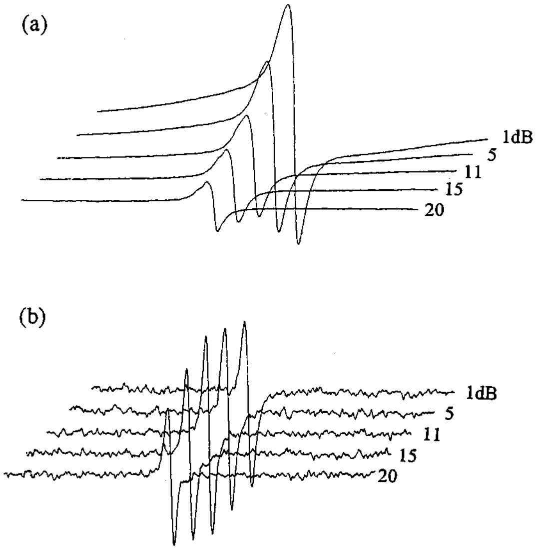
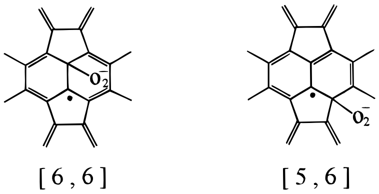


Figure 6. Microwave power saturation behavior of the bands (a) b ($g = 2.0008$) and (b) c ($g = 2.0026$) at room temperature in an air-saturated sample. The microwave power is labeled in the figure. A modulation of 1.5 G is used for both (a) and (b). The curved baseline in (a) is due to residual $C_{60}^{\bullet-}$ signal which has a short T_1 relaxation time and becomes significant at high microwave power conditions.

To obtain the relative magnitude of relaxation times of bands b and c, microwave power saturation experiments were conducted and the results and shown in Figure 6a and b. The peak height of band b (see Figure 6a)increases continuously at higher microwave powers. Examination of the double-integrated area of band b, however, shows a slightly deviation from a linear function of the square root of the microwave power (P) as P is stronger than 12 dB. This type of partial saturation pattern is different from that of the $C_{60}^{\bullet-}$ anion radical of which the increase in the signal area is a linear function of the square root of the microwave power at all microwave power range (up to 1dB, data not shown). Therefore, the relaxation times of band b are longer than those of the $C_{60}^{\bullet-}$ anion radical. This is consistent with the expection that oxygenation of the $C_{60}^{\bullet-}$ anion radical destroys the molecular symmetry, slows down molecular rotation, and results in larger relaxation times. Figure 6b shows that band c is more prone to microwave power saturation than band b. At microwave powers stronger than 25dB, the signal area of band c starts to deviate from the linear function of the

SCHEME 1



[6,6] [5,6]

square root of the microwave power. Therefore, the relaxation times of band c are even longer than those of band b.

Discussion

The decrease of the integrated intensities of the signals in Figure 1 as a function of time indicates that oxygenation of $C_{60}^{\bullet-}$ anion radical produces predominantly diamagnetic products.[34] The structures of the two paramagnetic species that are produced by the reaction are proposed to be the [6,6]- and [5,6]-ring junction isomers (see Scheme 1). In the studies of $RC_{60}^{\bullet}$ (R = alkyl) radicals, it was found[9] that the delocalization of the radical site is very poor, and the radical tends to locate at the carbon directly adjacent to the alkyl substituent. Although the [6,6] structure can be transformed to the [5,6] structure via delocalization of the radical site, they might not be equivalent, especially when complexed to the $[(ph)_3P]_2N^+$ countercation. In the literature, various C_{60} derivatives have been synthesized. Nearly all functionalization occurs at the [6,6]-ring junction.[3] Few examples happen at the [5,6]-ring junction.[35] Those results indicate that opening the double bond across the [6,6]-ring junction releases more strain and leads a more stable structure. Therefore, band c ($g = 2.0026$) was tentatively assigned to the [6,6] structure and band b ($g = 2.0008$) to the [5,6] structure. The quenching of $C_{60}^{\bullet-}$ anion radical by oxygen was reported to generate superoxide radical anion.[36] In the current system, two possible mechanisms could occur: namely, direct attachment of oxygen to the negatively charged site, and electron transfer to oxygen followed by addition of superoxide to the fullerene cage. Both mechanisms result in the formation of the [6,6] and [5,6] structures. The current ESR data cannot distinguish these two mechanisms.

The negative temperature dependence of the transformation rate of species b to c requires the existence of an intermediate, I, which is in preequilibrium with species b. That is

$$\mathrm{b} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{I} \underset{(k_{-2})}{\overset{k_2}{\rightleftharpoons}} \mathrm{c} \qquad \text{(II)}$$

The k_f obtained in the previous "temperature jump" experiment is actually equivalent to $(k_1/k_{-1})k_2$. Under low polar environments (e.g., 14.3% methanol in toluene), the transformation rate (k_{-2}) of c to I is too slow and is neglected from the eq II for the moment. Based on eq II, the disappearance rate, $-d[b]/dt = k_1[b] - k_{-1}[I]$, and $d[I]/dt = k_1[b] - (k_{-1} + k_2)[I]$. Under a steady-state condition, $[I]_{ss} = k_1[b]/(k_{-1} + k_2)$. Therefore, $-d[b]/dt = [k_1k_2/(k_{-1} + k_2)][b]$. The $[k_1k_2/(k_{-1} + k_2)]$ term is the k_{obs}. Since $k_2 \ll k_{-1}$ (preequilibrium), the k_2 term can be omitted from the denominator for simplicity. The k_{obs} is a function of both temperature (T) and the equilibrium ratio (K) of [I]/[b]. To have a negative temperature dependence, dk_{obs}/dT has to be negative. That is

$$\begin{aligned}\partial k_{obs}/\partial T &= [\partial k_{obs}/\partial T]_K + (\partial k_{obs}/\partial K)_T(\partial K/\partial T) \\ &= \frac{(E_{a1} + E_{a2} - E_{a-1})}{RT^2}\frac{k_1k_2}{k_{-1}} + \frac{(E_{a1} - E_{a-1})}{RT^2}\frac{k_1k_2}{k_{-1}} < 0\end{aligned} \qquad (1)$$

Rearrangement of eq 1 leads to

$$0.5E_{a2} + E_{a1} < E_{a-1} \qquad (2)$$

That is, the intermediate I should be thermodynamically more stable than the reactant b in order to have a negative temperature dependence of the disappearance rate of species b. Since E_{a2} is larger than E_{a-1}, the upper and lower limits of E_{a2} can also be obtained, i.e.,

$$E_{a-1} < E_{a2} < 2(E_{a-1} - E_{a1}) \qquad (3)$$

Equations 2 and 3 are the boundary condition for reaction II to have an inverse temperature dependence for the disappearance rate of the species b.[37] Physically, it is not difficult to understand the origin of the "negative temperature dependence" behavior. The major exit channel of b is via equilibrium with I, which then converts to the product c. High-temperature equilibrium causes decrease of I and increment of b, where b does not have any exit channel at all (or b has another very slow exit channel besides the I channel). Therefore, a higher temperature slows down the disappearance rate of b.

Currently, it is not clear what the precise structure of the intermediate I is, why the intermediate I does not show a ESR signal, and why the transformation of b to c shows a positive temperature dependence as $T < 328$ K. The absence of an ESR signal for the intermediate I could be due to very long T_1 relaxation time, many delocalization structures, or other unknown factors. Alternative possibility is that band b is a collapse band of two ESR signals from species b and intermediate I. The collapsing of two ESR (or NMR) bands occurs when the interconversion rate between two species is sufficiently fast. Kinetically, this assumption is not impossible. In this case, the disappearance rate of b plus I, $-d(b + I)/dt = [k_1k_2/(k_{-1} + k_2)][b]$. The k_{obs} is the same as that for the disappearance of species b alone. Therefore, the boundary condition for a negative temperature dependence of the disappearance of b plus I is the same as that for the disappearance of b. In other words, as long as eqs 2 and 3 are fulfilled, the disappearance rates of both b and (b plus I) will all show a negative temperature dependence. Physically, this is quite understandable. In the "pool" of b plus I, the component b is not reactive and the component I is reactive. At high temperatures, the equilibrium favors a larger fraction of the nonreactive component b, and therefore results in a reduced disappearance rate of the "pool" (i.e., b plus I). Experimentally, this has been observed in the decay of triplet biradicals,[28] of which the more reactive open chain and the less reactive closed chain forms are in fast equilibrium and indistinguishable. The above assumption that band b is a collapse band of species b and intermediate I, however, is not supported by experimental observations, since the line width of band b becomes narrower at lower temperatures (see Figure 5).[38]

Upon oxygenation, the symmetry of $C_{60}^{\bullet-}$ was reduced and molecular rotational rate slowed down. Therefore, $C_{60}O_2^{\bullet-}$ has much narrower line width(s) than the $C_{60}^{\bullet-}$ anion radical and is easily saturated by microwave power.[13b] Species c has a narrower line width and longer relaxation times than those of species b, indicating that species c is in a much more rigid environment than species b. The structures of the [6,6]- and [5,6]-$C_{60}O_2^{\bullet-}$ alone cannot account for the differences in the relaxation times and the ESR line widths. Complexation with the organic salt countercation has to contribute significantly to the rigidity of environments of the species b and c.

In the system of 30% methanol−toluene solution, the equilibrium ratio of b to c (~0.65 at 365 K) indicates that isomer c is thermodynamically more stable than isomer b by an amount of ~1.3 kcal/mol.

The spectra shown in Figure 1 resemble the spike commonly observed in $C_{60}^{\bullet-}$ ESR spectra, especially those reported by Moriyama et al.[18,39] As predicted by Eaton and co-workers,[13b] the spike is indeed due to a derivative of C_{60}. Since oxygen is a universal impurity in all laboratories, insufficient deoxygenation by argon purging often leads to the formation of the $C_{60}O_2^{\bullet-}$ anion radical. Due to their narrow line widths, the small amount of the $C_{60}O_2^{\bullet-}$ anion radical is readily observed. In the ESR measurements of C_{60}^{2-} and C_{60}^{3-}, a sharp, questionable band was also frequently observed. The peak height of this sharp band varies from sample to sample.[13b] It is very likely that this sharp band is also due to the oxygenated C_{60} anion radicals. It is worth reexamining these systems and taking into account the oxygen quenching problem. With these considerations, it will help to clarify whether the ground state of C_{60}^{2-} biradical is diamagnetic or triplet.[13,14] If the sharp spike in the C_{60}^{2-} ESR spectra is indeed due to the oxygenated C_{60} monoanion radical, the C_{60}^{2-} dianion will most probably be diamagnetic.

In the studies of photoexcitation of C_{60} in the presence of amines or TiO_2 colloids, Stasko and co-workers[40] observed a spike on top of a narrow $C_{60}^{\bullet-}$ band. They tentatively assigned the spike to be the C_{60}^{2-} dianion radical. Since their spectra are different from those commonly observed by many others[13−18] where the spike is on top of a broad $C_{60}^{\bullet-}\cdot$(organic salts) band, we believe that their spike has a different origin from the $C_{60}O_2^{\bullet-}$ reported here.

Conclusion

Our ESR data indicate that the spike commonly observed in the $C_{60}^{\bullet-}$ ESR spectrum is most probably due to oxygenation of the $C_{60}^{\bullet-}$ monoanion radical.[41] The oxygenated C_{60} anion radical exists as two interconvertible isomers. The isomer b ($g = 2.0008$; $\Delta H_{pp} = 3.32$ G) is a kinetic product, favored by polar environments, and has longer relaxation times than the $C_{60}^{\bullet-}$ anion radical. The isomer c ($g = 2.0026$; $\Delta H_{pp} = 1.67$ G) is a thermally more stable product, favored by nonpolar environment, and has much longer relaxation times than isomer b. The transformation rate of isomer b to c was found to be inversely temperature dependent. Kinetic analysis from a theoretical model shows that, to have a negative temperature dependence of a reaction rate, not only a fast equilibrated intermediate is required but also the intermediate has to be thermodynamically more stable than the reactant (i.e., $0.5E_{a2} + E_{a1} < E_{a-1}$).

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