Exergonic Electron-transfer Reaction Between [60]Fullerene Anion and Carbazole Cation

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The fluorescence of C_{60} is observed in the reaction of C_{60} radical anion and carbazole cation; this is interpreted in terms of the Marcus free energy diagram indicating a C_{60} intermediate triplet state.

Electron-transfer reactions in the photoexcited state of C_{60} have been investigated.[1,2] Photoexcited poly(*N*-vinylcarbazole) transfers its electron to C_{60} to produce its radical anion and poly(*N*-vinylcarbazole) cation.[1] Energetically this would be a favoured reaction [E_s = 2.01 E_T = 1.56[3] for C_{60} and $E_s \simeq$ 3.33 and E_T = 3.04 eV for poly(*N*-vinylcarbazole)[4]] as the redox potentials of $C_{60}/C_{60}^{-\cdot}$ and poly(*N*-vinylcarbazole)$^{+\cdot}$/poly(*N*-vinylcarbazole) are situated at −0.44 and +0.85 V *vs.* SCE.[5–8] The reverse reaction is endergonic and cannot produce an excited state of either of the reactants. In the light of the above results it would be of interest to consider a situation where a reverse exergonic electron-transfer reaction would produce an excited state of C_{60} by reacting C_{60} radical anion and unpolymerised carbazole cation or polymerised carbazole cation without any substituent, which is expected to have a higher redox potential than poly(*N*-vinylcarbazole).

Our previous studies[9,10] showed that unsubstituted carbazone (E_p = 1.35 V) has a redox potential which is located more positive than pol(*N*-vinylcarbazole).[8] The calculation of the energetics of the radical ion electron-transfer reaction between C_{60} and carbazole (Car) is sufficiently exergonic to populate the excited state of C_{60}. In order to examine the effectiveness of the electron transfer reaction between $C_{60}^{-\cdot}$and Car cation ($Car^{+\cdot}$), we applied Marcus theory of electron-transfer reactions to this situation.[11–13] In constructing the free-energy profiles, the radius (r) of C_{60} = 5.0 and Car = 4.39 Å were used in estimating the solvent reorganisation energy, λ = 0.596 eV. The electronic levels of Car: E_{S1} = 3.73 and E_{T1} = 3.04 eV[2,14,15] were used in the calculations. The free energy profiles for the reaction, suggests that the triplet state of C_{60} is accessable in the electron-transfer reaction between $C_{60}^{-\cdot}$ and $Car^{+\cdot}$. The barrier for the formation of all the other electronic states are very high and would not be effective. The excited singlet-state formation of C_{60} will then have to occur *via* triplet–triplet annihilation process.[7,13] Fig. 1 shows the Marcus diagrams for the above electron-transfer reaction.

The electron-transfer reaction between $C_{60}^{-\cdot}$ and $Car^{+\cdot}$ was experimentally carried out by electrochemically generating the above species in methylene chloride by a potential programming at a Pt working electrode[7,13] in a vacuum electrolytic cell. The CV curve for a solution containing Car and C_{60} in methylene chloride solvent with TBAP as the supporting electrolyte showed peaks at −0.44 and −0.88 V which are identified[5,7] as due to first and second reductions of C_{60} as shown by reactions (1) and (2).

$$C_{60} + e \rightleftarrows C_{60}^{-\cdot} \quad (1)$$

$$C_{60}^{-\cdot} + e \rightleftarrows C_{60}^{2-} \quad (2)$$

In addition to the above two peaks, a single reversible anodic peak situated at + 1.40 V (complementary cathodic peak at + 1.35 V) is observed due to the oxidation of Car and the reduction of its cation as shown by reaction (3).

$$Car \underset{}{\overset{-e}{\rightleftarrows}} Car^{+\cdot} \quad (3)$$

If a solution is prepared without Car in the medium, this peak was absent. The electrochemistry of Car has been well documented in the literature.[9,10,16,17] By potential pulsing between + 1.45 and − 0.60 V at 5 Hz the reaction between $C_{60}^{-\cdot}$ and Car^{+} was effected as shown by reaction (4)

$$C_{60}^{-\cdot} + Car^{+\cdot} \rightarrow C_{60}^{*} + Car \quad (4)$$

$$C_{60}^{*} \longrightarrow C_{60} + h\nu \quad (5)$$

The light pulses observed have the wavelength response as shown in Fig. 2. After a prologed pulsing (5 cycles) of the potential of the electrode in the above limit a black film is

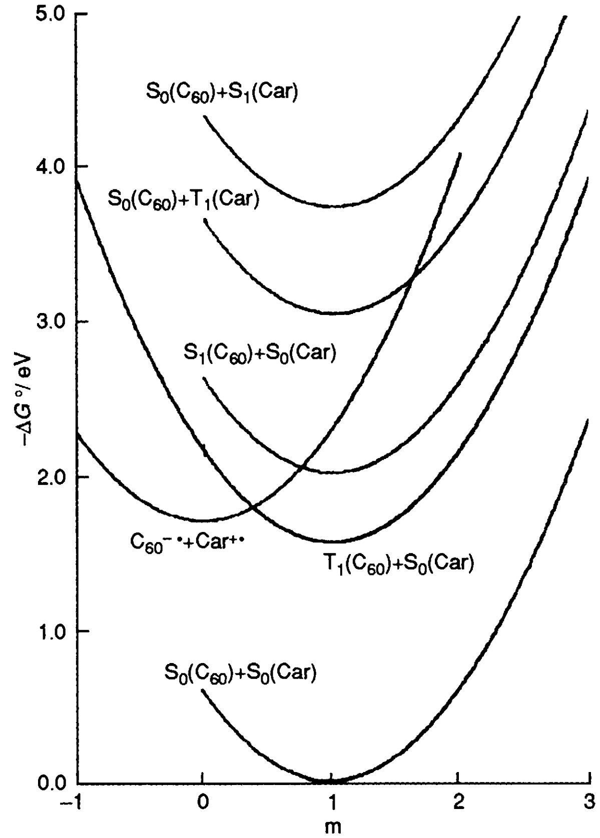

Fig. 1 Marcus diagram for the electron-transfer reaction between C_{60} radical anion and Car cation

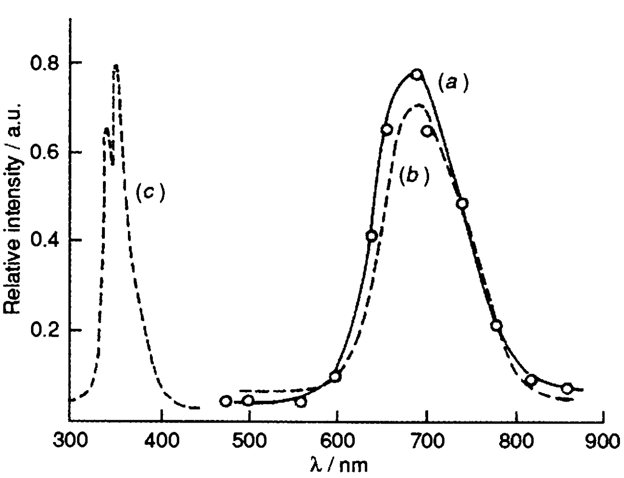

Fig. 2 (*a*) Emission spectrum obtained during the electron-transfer reaction between C_{60} and Car by pulsing the potential of the electrode between 1.40 and −0.60 V. The solution contained 0.5 mmol dm^{-3} C_{60} and 1.0 mmol dm^{-3} carbazole and 0.1 mol dm^{-3} $(C_4H_9)_4NClO_4$. (*b*) Fluorescence spectrum of C_{60}: ----. (*c*) The fluorescence spectrum of Car. Excitation wavelengths for C_{60} = 532 nm and Car = 290 nm.

observed which is attributed to the polycarbazole film.[14,15] Experiments were carried out in methylene chloride containing only C_{60} and the supporting electrolyte [Bu_4NClO_4] using the filmed electrode as the working electrode in the potential pulsing programme. The peaks due to C_{60} reductions were clearly visible in the CV recordings. By pulsing the potential between + 1.40 and − 0.50 V, light pulses were observed, but the intensity of these light pulses were about 1000 times less than in the previous experiment which contained Car. The spectral features in this experiment is identical to C_{60} fluorescence indicating that the oxidised state of the polycarbazole film takes the electron from $C_{60}^{-\cdot}$. Optical emission from carbon clusters have also been reported earlier[18] in a superionic expansion.

While the experiments described here clearly demonstrates the efficient electron-transfer reaction between $C_{60}^{-\cdot}$ and Car^{+}, the process of formation of the excited singlet state in reaction[4] cannot be a direct process as the free energy released in this reaction is only −1.78 eV (short of about 0.33 eV). Watanabe and Ito[1] discuss the possibility of heteroexcimer formation in the case of poly(*N*-vinylcarbazole) and C_{60} in benzonitrile but conclude that low fluorescence quantum yield of the exciplex precludes its observation in the experiments they have performed. In our experiments also we do not see any excimer emission possibly due to its fast decomposition into its products. Nevertheless, the results reported here demonstrate an efficient electron transfer occurring between C_{60} radical anion and carbazole cation or C_{60} radical anion and polycarbazole cation to produce the excited state of C_{60} which does not occur with C_{60} radical anion and poly(*N*-vinylcarbazole) cation.[1]

Received, 26th July 1994; Com. 4/04597A

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