A Facile and Selective Method for the Solution-phase Generation of C_{60}^- and C_{60}^{2-}

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The facile and selective generation of C_{60}^- or C_{60}^{2-} has been accomplished by treating C_{60} with alkyl thiolates in non-aqueous solvents of varying composition.

Although all six anions of buckminsterfullerene, C_{60}^{n-} (n = 1–6) have now been synthesized by electrochemical[1] or chemical methods,[2,3] there are very few reports in the literature describing a single method which can be used for the selective solution-phase chemical generation and isolation of a given C_{60}^{n-} species associated with a variety of different counter-cations. As part of our continuing efforts to study the physical properties of various fulleride salts[3] and to synthesize organofullerenes,[4] we have investigated the reaction of alkyl and aryl thiolates† with C_{60} in polar aprotic media. We found that this reaction with alkyl thiolates allows one to selectively generate either C_{60}^- or C_{60}^{2-} depending upon the solution conditions and this is reported in the present communication.

In a typical experiment, a few drops of propanethiol (PrSH) are added to a suspension of C_{60} and K_2CO_3 in dimethylformamide (DMF) while stirring under nitrogen. The colour of the mixture initially changes from colourless to green but then quickly yields an intense red solution. The near IR (NIR) optical absorption spectrum of the red solution has absorption bands at 945 and 829 nm [Fig. 1(*b*)] which are characteristic of the C_{60} dianion.[2b,6]‡ The EPR spectrum of the frozen (T = 112 K) red solution [Fig. 1(*b*) inset] is also characteristic of the C_{60} dianion[7a] and consists of a narrow line (g = 2.000, ΔH = 2.0 G) superimposed on a pair of spectral lines arising from a magnetic triplet. The EPR and NIR data of the red solution are thus self-consistent and can only be assigned to C_{60}^{2-}.

The chemical generation of C_{60}^{2-} under these experimental conditions can be rationalized by considering the relevant redox potentials for the two reagents. The $E_{1/2}$ of the $C_{60}^{0/-}$ and $C_{60}^{-/2-}$ couples in DMF are located at −0.26 and −0.72 V *vs.* SCE, respectively,[8] while propanethiolate (PrS⁻), generated from the reaction between PrSH and K_2CO_3 in DMF,[9] is oxidized at E_{pa} = −0.58 V *vs.* Ag–AgCl in acetonitrile to give the propanethiyl radical (PrS·).[10] This latter peak potential is shifted from the thermodynamic $E_{1/2}$ value (which is unknown) to more negative potentials due to the irreversible formation of dipropyldisulfide which removes PrS· from solution. The effective oxidation potential, shifted cathodically by the chemical reduction[11] (disulfide formation), then becomes sufficiently negative to reduce C_{60} to C_{60}^{2-}.

One of the most notable features of the electron-transfer reaction involving C_{60} and PrS⁻ is that either C_{60}^- or C_{60}^{2-} can be generated depending upon the exact solvent composition. For example, a green solution is immediately obtained when C_{60}, PrSH and K_2CO_3 are mixed in a 10:90 DMF–toluene mixture. The NIR spectrum of the product [Fig. 1(*a*)] has absorption bands at 1075 and 980 nm and these can be unambiguously assigned to the C_{60} monoanion.[2b,6] The room-temperature EPR spectrum of this green solution [Fig. 1(*a*) inset] has a broad line (ΔH = 69 G) at g = 1.999 and is also characteristic[7b] of C_{60}^-.

The colour of the product becomes increasingly reddish when the ratio of DMF to toluene in the mixture is increased above 10% and, under these conditions, both the EPR and the NIR spectra show that increasing amounts of C_{60}^{2-} are produced (the 945 nm band of the product in the NIR increases in intensity while that of the 1075 nm band decreases). The EPR and NIR spectra of the final dark red product obtained in neat DMF [Fig. 1(*b*)] shows that C_{60}^{2-} is formed. Neither the EPR nor the NIR spectrum shows the presence of any C_{60}^- in this red solution. These results thus indicate that the reaction between C_{60} and PrS⁻ in neat DMF gives first C_{60}^-, which is green in colour, followed by C_{60}^{2-}, which is red.

The relationship between the final product (C_{60}^{2-} or C_{60}^-) and the DMF : toluene ratio can also be explained on the basis of the $C_{60}^{n-/(n+1)-}$ redox potentials. As described above, the apparent potential of the PrS⁻/PrS· couple in neat DMF is sufficiently negative to generate C_{60}^{2-} from C_{60} *via* an overall two-electon transfer. However, the half-wave potential of the $C_{60}^{0/-}$ and $C_{60}^{-/2-}$ couples in solutions containing a large excess of toluene (10% DMF and 90% toluene) are shifted cathodically by 70–80 mV with respect to the $E_{1/2}$ values in neat DMF, and are then located at −0.34 and −0.79 V (*vs.* SCE),[12] respectively. Under these latter solution conditions, the potential of the PrS⁻/PrS· couple seems to not be sufficiently negative to produce C_{60}^{2-} although it can produce C_{60}^-.

Finally, it should be noted that a number of non-aqueous solvents can also be used for the synthesis of either C_{60}^- or C_{60}^{2-} provided that the reduction potential of the desired

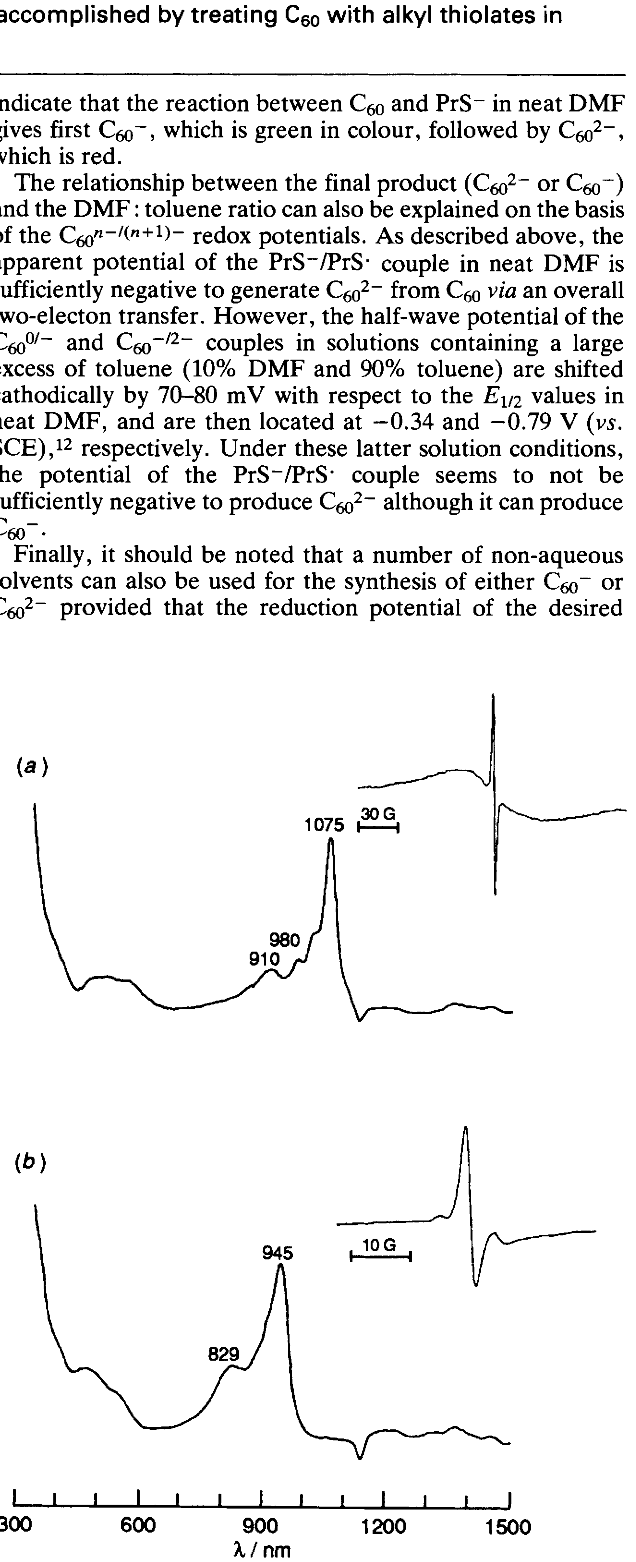

Fig. 1 NIR spectra of (*a*) C_{60}^- and (*b*) C_{60}^{2-} generated by reaction of PrS⁻ and C_{60}. Insets show EPR spectra of (*a*) C_{60}^- at 298 K; the narrow line superimposed upon the EPR spectrum of C_{60}^- is assigned to the C_{60}^{2-} dianion[7] and accounts for <1% of the paramagnetic species in the sample and (*b*) C_{60}^{2-} at 112 K; the dianion accounts for >99% of the unpaired spins in this sample.

$C_{60}^{n-/(n+1)-}$ couple can be reached with the given alkyl thiolate in the utilized solvent. For example, only C_{60}^- is formed in neat THF whereas the doubly reduced C_{60}^{2-} is formed in neat acetonitrile (MeCN) using caesium carbonate as the base. (This example is given since the potassium salts of C_{60}^- and C_{60}^{2-} are insoluble in MeCN). Under our experimental conditions, the use of thiophenolate (PhS^-) does not produce either C_{60}^- or C_{60}^{2-}. Presumably the oxidation potential of the $PhS^-/PhS^\cdot$ couple is more positive than that of the $PrS^-/PrS^\cdot$ one due to a resonance stabilization of PhS^-.

In conclusion, C_{60} mono- and di-anions can be generated by reacting C_{60} with PrS^- in a mixture of DMF and toluene with the specific product (C_{60}^- or C_{60}^{2-}) depending upon the specific DMF–toluene ratio. Efforts are now underway to use this method in order to synthesize and characterize new organofullerenes by reacting C_{60}^{2-}, generated selectively by the above described thiolate method, with a variety of electrophiles.

The financial support of the Robert A. Welch Foundation (E-680, K. M. K. and E-1208, M. T. J.), The Texas Center for Superconductivity at The University of Houston (TCSUH) and the Energy Laboratory, University of Houston, are gratefully acknowledged.

Received, 4th May 1994; Com. 4/02656J

Footnotes

† Thiolates are known to form disulfides irreversibly, and are hence good reducing agents.[5]

‡ No absorption bands were observed in the NIR spectra of either the propanethiolate or the neutral C_{60} under the same solvent conditions.

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