Single-electron reduction of C_{60} with a carbon radical: formation of the Crystal Violet cation–fulleride ion salt†

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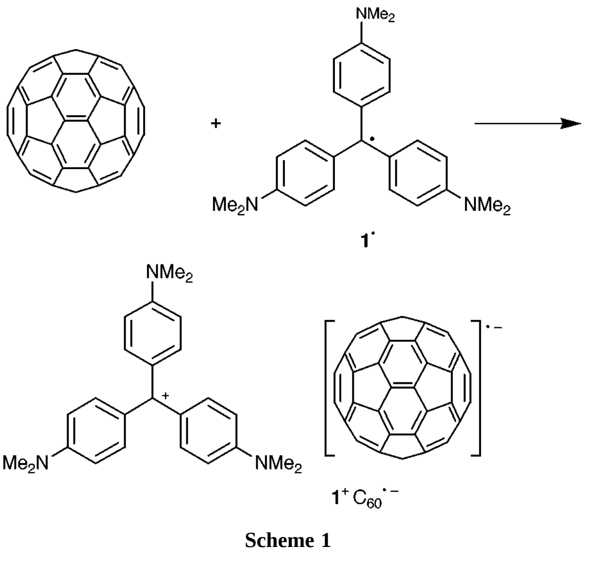
Whereas many carbon radicals are known to add to C_{60}, the reaction of Crystal Violet radical $\mathbf{1}^{\bullet}$ with C_{60} resulted in single-electron transfer, leading to a carbocation–carbanion salt $\mathbf{1}^{+}C_{60}^{\bullet-}$: the product was isolated as microcrystalline powder and was characterized by EPR, VIS-NIR and NMR spectroscopy.

The addition of radicals to buckminsterfullerene (C_{60}) to give fullerenyl radicals constitutes a well-known and characteristic reaction. The addition of reactive carbon-centered radicals, such as alkyl, benzyl and haloalkyl radicals and some heteroatom-centered radicals, to C_{60} has been reported to produce $RC_{60}^{\bullet}$ as well as multiple-addition fullerenyl radicals.[1] The high affinity of C_{60} toward radicals has been demonstrated by its ability to absorb up to 34 methyl radicals,[2] 15 benzyl radicals,[2] 11 phenyl radicals,[3] and 16 perfluoroethyl radicals.[4] Another possibility in the reaction of an alkyl radical with C_{60} is electron transfer from the radical to C_{60}. Such a reaction, which, to the best of our knowledge, has not been reported, would be expected to occur if the reducing power of the radical is sufficiently strong to reduce C_{60}. We report herein the single-electron reduction of C_{60} with the Crystal Violet radical $\mathbf{1}^{\bullet}$ and the isolation of the product $\mathbf{1}^{+}C_{60}^{\bullet-}$ as a solid (Scheme 1).

For stoichiometric single-electron transfer from a carbon-centered radical $R^{\bullet}$ to C_{60} without a subsequent redox or chemical process, the following requirements must be fulfilled. First, the oxidation potential of $R^{\bullet}$ must be more negative than the first reduction potential of C_{60} (-1.09 V *vs.* Fc/Fc^{+}),[5] but not more negative than the second reduction potential (-1.48 V *vs.* Fc/Fc^{+}).[5] Considering the effective delocalization of the positive charge in $\mathbf{1}^{+}$ over three nitrogen atoms, one would expect that the corresponding radical $\mathbf{1}^{\bullet}$ would be readily oxidized. Cyclic voltammetry for $\mathbf{1}^{+}I^{-}$ indicates that the $\mathbf{1}^{\bullet}/\mathbf{1}^{+}$ redox couple has a potential of -1.19 V *vs.* Fc/Fc^{+} in PhCN, which is midway between the first and second reduction potentials, thus allowing a complete single-electron reduction to give $C_{60}^{\bullet-}$ but no further electron transfer to C_{60}^{2-}.[6] Secondly, the ions produced by the electron transfer, R^{+} and $C_{60}^{\bullet-}$, should be sufficiently stable so as not to react with each other. Although carbocations and carbanions have a strong tendency to combine to form neutral molecules, we have earlier reported that a highly stabilized carbocation with a $pK_{R^{+}}$ of 7.29–13.6 and a carbanion whose conjugate acid has a pK_a of 5.7–5.9 can, in fact, coexist in solution and in the solid state, without cation–anion coordination.[8] The reported $pK_{R^{+}}$ of $\mathbf{1}^{+}$ (9.36[9]) and the pK_a of the conjugate acid of $C_{60}^{\bullet-}$ (3.4–9.0[10]) led to the prediction that these ions are sufficiently stable to allow the formation of a stable salt, $\mathbf{1}^{+}C_{60}^{\bullet-}$, rather than a neutral radical, $\mathbf{1}$–$C_{60}^{\bullet}$. In addition, the formation of such a bond would be severely hindered, because of the repulsion between the aromatic rings of $\mathbf{1}^{+}$ and the fullerene cage.



Scheme 1

Radical $\mathbf{1}^{\bullet}$ can be quantitatively generated by the reduction of the Crystal Violet cation $\mathbf{1}^{+}$ with zinc.[11] Unlike the unsubstituted triphenylmethyl radical, this radical does not dimerize but persists in solution.[12] All the procedures for the preparation of $\mathbf{1}^{+}C_{60}^{\bullet-}$ and spectroscopic analysis of the product were carried out under degassed conditions using a glass apparatus connected to a high-vacuum line ($<10^{-4}$ mmHg). The apparatus contains two chambers, one for the preparation of $\mathbf{1}^{\bullet}$ and the other for the reduction of C_{60}. The two chambers are separated by a sintered glass frit, and to the latter is connected a tube or a cell for spectroscopic analysis of the product. In a typical experiment, $\mathbf{1}^{\bullet}$ was prepared by the treatment of anhydrous Crystal Violet iodide (2.05 mg) with zinc powder (93 equiv.) in 0.1 ml of pyridine. The zinc iodide was precipitated as the pyridine complex by diluting the reaction mixture with hexane (1.2 ml). The resulting red solution of $\mathbf{1}^{\bullet}$ was then transferred to the other chamber, which contained a CS_2 solution (5 ml) of C_{60} (2.86 mg, 0.97 equiv.). The salt $\mathbf{1}^{+}C_{60}^{\bullet-}$ was immediately precipitated from the mixed solution as red–brown microcrystalline powder, which was collected on the sintered glass frit and washed three times with small amounts of CS_2. Elemental analysis of the crystals[13] showed a nitrogen content of 3.50%, a value close to that calculated for $\mathbf{1}^{+}C_{60}^{\bullet-}$ (3.84%), consistent with the 1:1 molar ratio of the Crystal Violet moiety and the C_{60} component.

The EPR spectrum for a powder sample showed a broad single line ($g = 1.999$, peak-to-peak width 2.9 mT at 20 °C). The signal intensity, relative to a known amount of external standard, 4-hydroxy-TEMPO, indicated that the solid contained 90 ± 10% of the theoretical amount of unpaired spins. A THF solution of the solid material showed spectra typical of the fullerene anion (Fig. 1). A broad signal (peak-to-peak width *ca.* 9 mT) with a superimposed spike (peak-to-peak width 1 mT, $g = 2.000$) was observed at room temperature; the former became narrower with decreasing temperature. These observations are all in agreement with the behavior of the $C_{60}^{\bullet-}$ signal reported earlier.[14,15]

A ^{1}H NMR spectrum, taken in CD_2Cl_2, showed the presence of $\mathbf{1}^{+}$ and the corresponding alcohol $\mathbf{1}$–OH in 41:59 molar ratio.

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† Experimental details and the ^{1}H NMR data for $\mathbf{1}^{+}C_{60}^{\bullet-}$ are available as supplementary data from the RSC web site, see http://www.rsc.org/suppdata/cc/1999/1529/

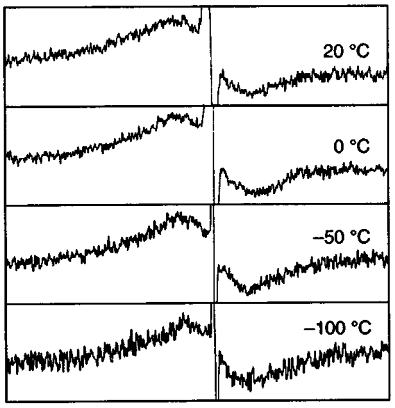
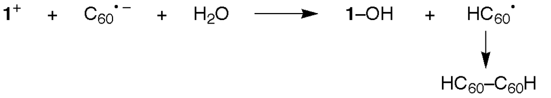


Fig. 1 X-Band EPR spectra of $\mathbf{1}^+C_{60}^{\bullet-}$ in THF recorded at 0.6 mW microwave power, 0.4 mT modulation and 50 mT sweep width.

The signals of $\mathbf{1}^+$ were significantly broadened, probably due to the paramagnetism of $C_{60}^{\bullet-}$. Hydrolysis by a trace amount of water in the solvent appears to be responsible for the formation of alcohol, indicating that the salt $\mathbf{1}^+C_{60}^{\bullet-}$ is extremely moisture-sensitive. This is in contrast to the fact that the other Crystal Violet salts, *e.g.* $\mathbf{1}^+Cl^-$, are stable in water. The difference may be explained by the higher basicity of $C_{60}^{\bullet-}$ compared with Cl^- and the dimerization of the resulting radical $HC_{60}^{\bullet}$ (Scheme 2).[16]



$$\mathbf{1}^+ + C_{60}^{\bullet-} + H_2O \longrightarrow \mathbf{1}\text{–OH} + \underset{\substack{\downarrow \\ HC_{60}\text{–}C_{60}H}}{HC_{60}^{\bullet}}$$

Scheme 2

The VIS-NIR spectrum of a THF solution of $\mathbf{1}^+C_{60}^{\bullet-}$ exhibited absorption maxima which were characteristic of $\mathbf{1}^+$ and $C_{60}^{\bullet-}$ at 593 and 1074 nm, respectively (Fig. 2). The latter absorption band had a substructure identical with that reported for $C_{60}^{\bullet-}$.[15,17] Based on the molar absorptivity of $\mathbf{1}^+$ at 593 nm (1.05×10^5 M^{-1} cm^{-1}) and assuming a 1:1 composition of $\mathbf{1}^+$ and $C_{60}^{\bullet-}$,[18] the molar absorptivity of $C_{60}^{\bullet-}$ at 1074 nm was calculated to be 1.96×10^4 M^{-1} cm^{-1}, which is comparable with reported values of 1.20–2.00 $\times 10^4$ M^{-1} cm^{-1}.[15c,17] The observed absorption line shape is in agreement with the sum of the independently measured absorptions of $\mathbf{1}^+$ and $C_{60}^{\bullet-}$. No significant decay of absorbance was observed, indicating the absence of charge recombination. Charge-transfer type interaction is also unlikely, since no absorption band indicative of a charge-transfer complex was observed.

The above experiments clearly demonstrated that C_{60} undergoes single-electron reduction by an electron-rich, sterically protected radical $\mathbf{1}^{\bullet}$. The product, $\mathbf{1}^+C_{60}^{\bullet-}$, is stable both in solution and in the solid state, providing a new isolated carbocation–carbanion salt. Thus, the possibility of electron-transfer in the reaction of organic radicals to C_{60} has been demonstrated as an alternative to the addition to C_{60}, which is usually observed for reactive radicals.

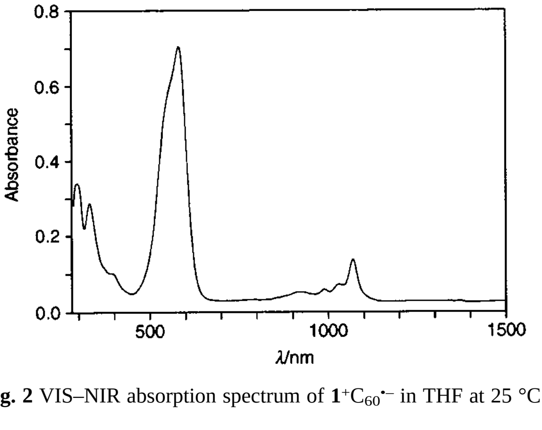


Fig. 2 VIS–NIR absorption spectrum of $\mathbf{1}^+C_{60}^{\bullet-}$ in THF at 25 °C.

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Notes and references

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18 Trace amounts of water in THF may also cause partial hydrolysis, which gives rise to **1**–OH. However, the 1:1 ratio would be retained, since the same amount of $C_{60}^{\bullet-}$ would be converted to HC_{60}–$C_{60}H$. **1**–OH and HC_{60}–$C_{60}H$ would be expected to have only a weak ($\varepsilon < 10^3$) absorption at wavelengths above 500 nm.

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