

Remarkable stability of $C_{60}^{\cdot-}$ in micelles

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We show that the lifetime of $C_{60}^{\cdot-}$ photochemically generated in a micellar medium is unusually long; of the order of minutes.

The formation $C_{60}^{\cdot-}$ by photoinduced electron transfer to triplet C_{60} has been demonstrated using a range of electron donors including aromatic amines.¹ Early work by Hochstrasser and coworkers indicated that in non-polar hydrocarbon solvents the radical ion pair generated by electron transfer does not separate but rather undergoes back-electron transfer. The lifetime of the radical ion pair formed by the reaction of triplet C_{60} with dimethylaniline in toluene was found to be < 1 ns.² Using more polar solvents encourages ion separation, for example in alcohol solution the $C_{60}^{\cdot-}$ ion has a lifetime of *ca.* 100 μ s. Hungerbuhler and coworkers have studied preparations of C_{60} in micellar and cyclodextrin solution and observed lifetimes of up to 440 μ s.³ Using UV-VIS spectroscopy and SANS† we have recently established that well defined C_{60} dispersions can be formed using non-ionic surfactant micelles. Of particular interest are those containing monomeric fullerene.⁴ Here these systems have been used to study the generation of $C_{60}^{\cdot-}$ by photoinduced electron transfer from ascorbic acid and to monitor the stability of the fullerene radical anion.

Samples containing monomeric C_{60} were prepared by the toluene evaporation method using C_{60} ($3.2 \mu\text{mol dm}^{-3}$) in 2% v/v aqueous reduced Triton X-100, TXR-100,‡ where $Z = [C_{60}]/[\text{surfactant}] = 1.5 \times 10^{-4}$. Solutions were degassed by the freeze-pump-thaw method. The laser flash-photolysis apparatus has been described elsewhere³ (10 ns pulses of 308 nm radiation with 0.05–1.0 mJ per pulse). Spectra of the long-lived radical anion were obtained using an ATI-Unicam UV-2 spectrometer. The filtered output of a camera flash gun was used to irradiate the samples *in situ*.

The triplet state of C_{60} in TXR-100 was quenched by ascorbic acid. The decay of the triplet state, probed at 750 nm, followed first-order kinetics and the observed rate constant matched the appearance of the radical-anion absorption band at 1070 nm. The quenching rate constant, k_Q , was determined by plotting k_{obs} vs.

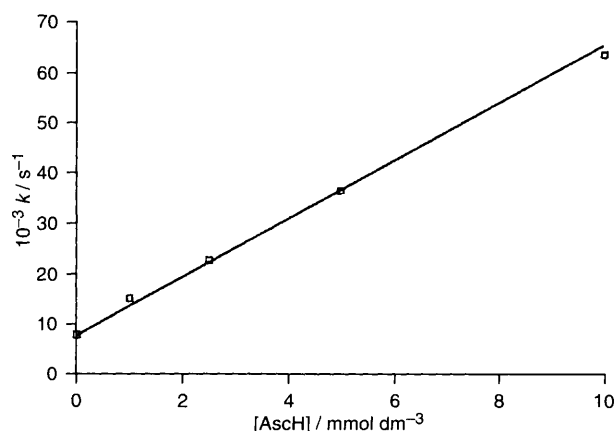


Fig. 1 Stern-Volmer plot of k_{obs} vs. ascorbic acid concentration used to calculate k_Q

[ascorbic acid] and $k_Q = 5.8 \pm 0.3 \times 10^6 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$; this data is illustrated in Fig. 1. This relatively low value is believed to arise due to the rather hydrophilic ascorbic acid remaining in the aqueous phase, away from the hydrophobic C_{60} which is expected to reside inside the micellar core. Similar rates have been observed for ascorbate reacting with tocopheroxyl radicals in micelles.⁵ The fullerene anion was observed to be very long lived and the decay was beyond the time range of the flash-photolysis apparatus. Therefore, experiments were carried out using a scanning UV-VIS spectrometer, which showed the lifetime of the radical ions to be in excess of 2 min; an accurate value is rather difficult to obtain given the need to completely exclude oxygen from the solution. The difference spectra obtained after irradiation of a sample are illustrated in Fig. 2. Interestingly the radical anion decays back to the aggregated form of C_{60} rather than the monomeric material as shown by the depletion of the spike at 406 nm and the appearance of new, broad bands at *ca.* 410 and 520 nm. This may be due to the fact that the data was obtained using solutions with a high Z value (1.4×10^{-4}) which are known to aggregate with time.⁴

Irradiation of aerated solutions of C_{60} in TXR-100 with ascorbic acid also resulted in the formation of the radical anion; the electron-transfer reaction of the triplet state is in competition with the quenching of the triplet fullerene by oxygen. Excitation of a solution containing 10 mmol dm^{-3} ascorbate generated a significant amount of the radical anion which decayed with a lifetime of 250 ms. From this data we have calculated the rate of the reaction $C_{60}^{\cdot-}$ with O_2 to be $(8 \pm 1) \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. The lifetime of the radical anion produced by ascorbic acid in these non-ionic surfactant micelles is very long compared to that produced by transfer from DABCO (1,4-diazabicyclo[2.2.2]octane; $\tau = 12$ ms).³ We suggest that this arises due to the low probability of back-electron transfer from the $C_{60}^{\cdot-}$ (encapsulated in the micelles) to the neutral dehydroascorbate (continuous aqueous phase). The radical cation of DABCO should also preferentially locate in the water; however, the

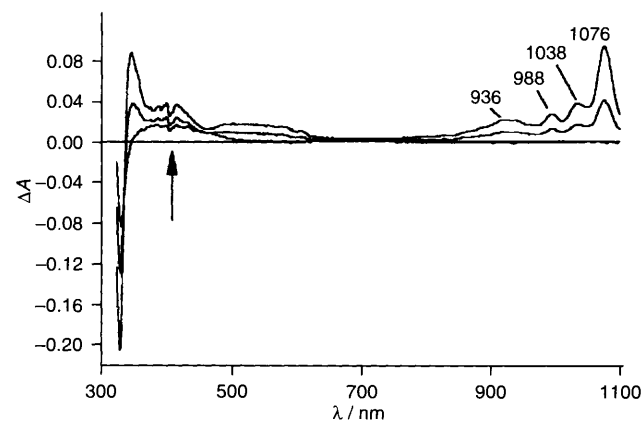


Fig. 2 UV-VIS-NIR absorption difference spectra obtained (a) 30, (b) 210 and (c) 600 s after irradiation of a solution of C_{60} in degassed TXR-100 containing 10 mmol dm^{-3} ascorbic acid. The bleach of C_{60} is observed at 330 and 405 nm and the bands due to the radical anion are seen at 350–450 and 950–1090 nm.

electrostatic interaction between the two species is expected to encourage back-electron transfer. The long lifetime of $C_{60}^{\cdot-}$ reported here is also surprising given the typical micelle lifetime τ_{mic} . Initial stopped-flow experiments have indicated that τ_{mic} for TXR-100 is of the order of 1–5 s, far less than that observed for the $C_{60}^{\cdot-}$. We propose that there may be some stabilising effect of the fullerene on the micelles.

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Footnotes

† SANS = small angle neutron scattering.

‡ Reduced Triton X-100 is a non-ionic surfactant $Me_3CCH_2CMe_2-C_6H_{10}O(CH_2CH_2O)_nH$, ($n = 8-10$). The alkyl and polyethylene oxide chains are in the 1,4 positions of the cyclohexane ring. Its cmc has been

determined by us to be the same, within experimental error, as Triton X-100, $cmc = 2.4 \times 10^{-4} \text{ mol dm}^{-3}$.

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