Radical-induced Redox and Addition Reactions with C_{60} Studied by Pulse Radiolysis

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Pulse radiolysis is introduced as a suitable general tool for investigating elementary redox and radical reactions of fullerenes in solution; absolute rate constants for such processes are reported.

Since the first successful synthesis of C_{60} by Krätschmer *et al.*[1] a steadily increasing number of studies have been conducted on this most interesting molecule. Redox chemistry studies, particularly by means of electrochemical methods,[2–6] have revealed the ability of fullerenes to accommodate up to six electrons in sequential reversible reduction steps.[4] Reversible oxidation, however, appears to be restricted to a one-electron process, yielding the $C_{60}{}^{\bullet +}$ radical cation[2] with spectral evidence for this species being provided by low-temperature matrix γ-irradiation[7] as well as by a photochemical study.[8] A further significant feature of C_{60} appears to be its capacity to add radicals at its double-bond system as could be deduced from ESR experiments[9–11] and a recent pulse-radiolysis study.[12] In this communication we demonstrate that radiation chemical methods are a most suitable tool for the investigation of free radical reactions with C_{60} and report, in particular, on one-electron redox reactions as well as on radical-addition processes. The results also include absolute rate constants for several of these reactions.

Pure C_{60} was purchased from Kaesdorf (Geräte für Forschung und Industrie, München, Germany). Solutions were generally freshly prepared before use. Whenever the degree of C_{60} dissolution was in question concentrations of C_{60} were determined spectrophotometrically by comparison with authentic samples of known concentration and in reference to published extinction coefficients.[7,13] The pulse-radiolysis experiments were performed by utilizing either 0.5–2 μs pulses of 1.55 MeV, or 500 ns pulses of 3.8 MeV electrons from two van de Graaff accelerator facilities, respectively. Details of the equipment and the analysis of data have been described elsewhere.[14,15] The radical concentration generated per pulse was typically (1–3) × 10^{-6} mol dm^{-3}. Steady-state radiolysis was carried out within the field of a ^{60}Co γ-source at a dose rate of 22 Gy min^{-1} (1 Gy = 1 J kg^{-1}). All experiments were carried out at room temp. (22 ± 2 °C).

Pulse radiolysis of a 3 × 10^{-5} mol dm^{-3} C_{60} solution in N_2O-saturated propan-2-ol leads to changes in optical absorption (ΔA), which are stable over the entire experimental timescale, *i.e.* for at least 10 ms. (Steady-state γ-radiolysis indicates stability even for hours in the absence of oxygen.) The differential spectrum recorded 150 μs after the 1 μs pulse is displayed in Fig. 1. Since it resembles the spectral changes obtained in a thin layer spectroelectrochemical reduction experiment[3] our radiation chemical process is suggested to be the one-electron reduction of C_{60} by the propan-2-ol radical [eqn. (1)]. The propan-2-ol radicals are known to be the only

$$C_{60} + Me_2C^{\bullet}(OH) \rightarrow C_{60}{}^{\bullet -} + Me_2CO + H^+ \qquad (1)$$

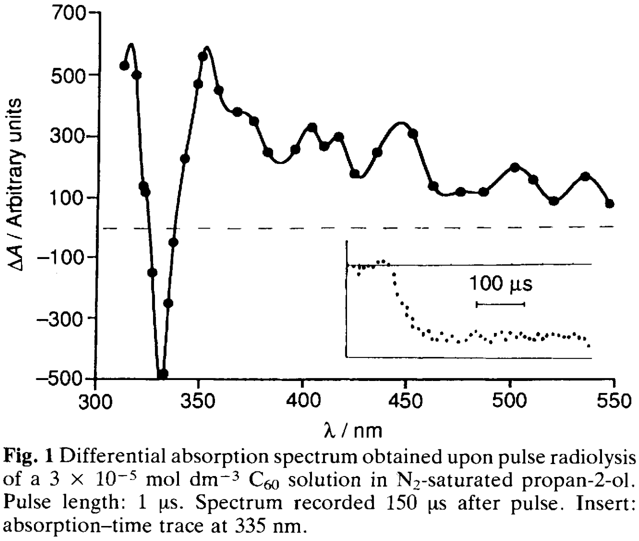

Fig. 1 Differential absorption spectrum obtained upon pulse radiolysis of a 3 × 10^{-5} mol dm^{-3} C_{60} solution in N_2-saturated propan-2-ol. Pulse length: 1 μs. Spectrum recorded 150 μs after pulse. Insert: absorption–time trace at 335 nm.

reactive species available for such a reduction reaction in N_2O-saturated solutions.[14] The time-resolved bleaching of the C_{60} absorption (recorded at 335 nm), for example, is shown in the insert of Fig. 1. Kinetic analysis of this trace, and respective time profiles at other wavelengths showing the formation of $C_{60}{}^{\bullet -}$, yielded an absolute rate constant for this reduction process of $k_1 = 5\ (\pm 2) \times 10^8$ dm^3 mol^{-1} s^{-1}. This rate constant is of the same order of magnitude as those for many other fast reductions by propan-2-ol radicals.[16]

Practically the same overall spectral changes have been obtained with propan-2-ol solutions saturated with N_2 instead of N_2O. Hence, the solvated electrons would not be scavenged by N_2O and (*via* $^\bullet$OH) converted into propan-2-ol radicals[14] but directly react with the fullerene, eqn. (2). In this case the

$$C_{60} + e^-_{sol} \rightarrow C_{60}{}^{\bullet -} \qquad (2)$$

time-resolved traces are separated into two distinguishable steps with the faster one referring to reaction (2). Owing to experimental limitations only a lower limit of $k_2 \geqslant 10^{10}$ dm^3 mol^{-1} s^{-1} can be given at present for the obviously diffusion-controlled electron attachment to C_{60}.

Preparation of a water-soluble C_{60}-complex has recently been achieved by generating a C_{60}–γ-cyclodextrin (γ-CD) host–guest complex in which the fullerene is suggested to be embedded into two molecules of γ-CD.[17] A pulse-radiolytic experiment has now been carried out with an N_2O-saturated, 9:1 (vol%) H_2O propan-2-ol solvent mixture containing various concentrations of this C_{60}–γ-CD complex. (The maximum γ-CD concentration was 1.7×10^{-3} mol dm^{-3}.) The only reducing radical available for reaction with C_{60} upon irradiation of such a system is again the propan-2-ol radical. The reduction of the fullerene within the host–guest complex occurs, however, more slowly than in the uncomplexed form. The bimolecular rate constant, now referring to eqn. (3) has

$$C_{60}\text{–}\gamma\text{-CD} + Me_2C^\bullet(OH) \rightarrow C_{60}{}^{\bullet -}\text{–}\gamma\text{-CD} + Me_2CO + H^+ \qquad (3)$$

been evaluated to be $k_3 = (2.7 \pm 0.5) \times 10^8$ dm^3 mol^{-1} s^{-1}. The slight slow-down of the electron transfer as compared with the neat propan-2-ol solution may, at least in part, be ascribed to the steric shielding provided by γ-CD although other parameters such as solvation and polarity of the solvent may also have to be considered for a quantitative interpretation.

One-electron oxidation of C_{60} could be achieved by irradiation of 1,2-dichloroethane (1,2-DCE) solutions. This solvent is known to generate highly oxidizing $(1,2\text{-DCE})^{\bullet +}$ radical cations.[18–23] Pulse radiolysis of an N_2-saturated 1,2-DCE solution of 4×10^{-5} mol dm^{-3} C_{60} yielded spectral changes that include some seemingly characteristic IR absorption features found in two other systems.[7,8] The near-IR part of the transient spectrum recorded in our experiment almost immediately after a 500 ns pulse is shown in Fig. 2. It resembles in particular the more resolved of the published $C_{60}{}^{\bullet +}$ spectra[8] with a major maximum at 980 nm and possibly another smaller one on the high energy side around 960 nm. We, therefore, assign this near-IR absorption to the fullerene radical cation formed *via* eqn. (4). It is not apparent to us why

$$(1,2\text{-DCE})^{\bullet +} + C_{60} \rightarrow C_{60}{}^{\bullet +} + 1,2\text{-DCE} \qquad (4)$$

this characteristic absorption band could not be detected in the recently published pulse-radiolysis study on C_{60} solutions in CCl_4 in which the authors also concluded, although only indirectly, on the formation of $C_{60}{}^{\bullet +}$ radical cations.[12] Possibly, this is a question of the particular solvent used since in our own experiments we noticed a significant dependence of the observable $C_{60}{}^{\bullet +}$ yields on the nature of the solvent.[24]

The formation of the $C_{60}{}^{\bullet +}$ absorption at 980 nm was practically complete at the end of the pulse. This allows an estimate of a lower limit for the bimolecular rate constant for the C_{60} oxidation of $k_4 \geqslant 2 \times 10^{10}$ dm^3 mol^{-1} s^{-1} to be made.

Additional support for our spectral assignment is provided by the lifetime of the 980 nm absorption, which closely agrees with that observed in the photochemical experiment.[8] The measured $t_{1/2}$ = 3.3 μs for the exponential decay process corresponds to a first-order decay rate constant of 2.1×10^5 s^{-1}. It should be noted though that the absorption–time trace displayed in the insert of Fig. 2 shows some significant residual absorption after the fast initial decay while the corresponding trace observed in the photochemical system decayed completely back to the original baseline.[8] The nature of this additional long-lived transient (it decays by second-order kinetics in the millisecond time domain), and whether or not it relates directly to the radical cation is not yet clear. Further investigations are underway.[24]

The third type of reaction to be addressed, besides reduction and oxidation, is radical addition. Pulse radiolysis of an N_2-saturated propan-2-ol solution containing 2×10^{-5} mol dm^{-3} C_{60} and 10^{-1} mol dm^{-3} MeI as electron scavenger induces spectral changes in the near-UV–VIS, which, monitored at maximum development of the transient absorption about 300 μs after the 1.5 μs pulse, are shown in Fig. 3.

This differential spectrum is seen to differ significantly from that obtained in the absence of methyl iodide (Fig. 1). Most important, no bleaching is observed at *ca.* 335 nm but rather a remarkable increase in absorption, as can also be recognized from the time-resolved trace displayed in the insert of Fig. 3 in comparison with the insert of Fig. 1.

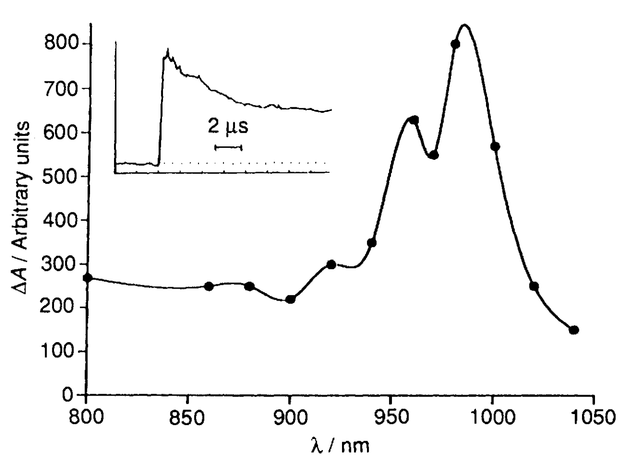

Fig. 2 Transient absorption spectrum recorded in the near-IR immediately after a 500 ns pulse in an N_2-saturated solution of 4×10^{-5} mol dm^{-3} C_{60} in 1,2-dichloroethane. Insert: absorption–time trace at 980 nm.

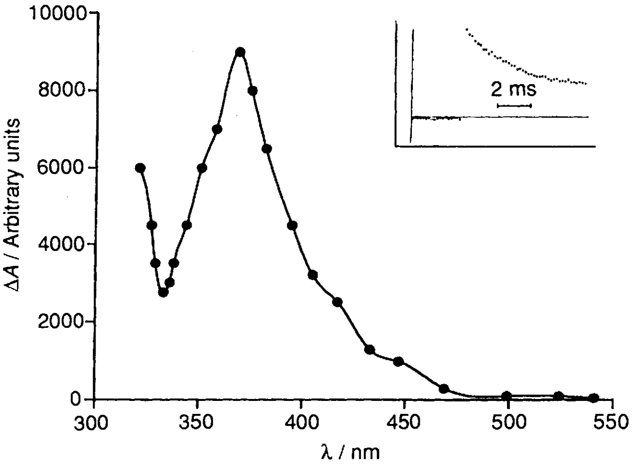

Fig. 3 Differential absorption spectrum obtained upon pulse radiolysis of a 2×10^{-5} mol dm^{-3} C_{60} solution in N_2-saturated propan-2-ol containing also 10^{-1} mol dm^{-3} MeI. Pulse length: 1.5 μs. Spectrum recorded *ca.* 300 μs after pulse. Insert: absorption–time trace at 335 nm.

The new species, which shows this relatively strong absorption with a maximum at 370 nm, is suggested to be the methyl radical adduct formed *via* the reaction sequence, eqns. (5) and (6). The adduct radical decays by second-order kinetics with a

$$\mathrm{MeI} + \mathrm{e^-_{sol}} \rightarrow {}^{\bullet}\mathrm{Me} + \mathrm{I^-} \qquad (5)$$

$${}^{\bullet}\mathrm{Me} + \mathrm{C_{60}} \rightarrow (\mathrm{C_{60}{-}Me})^{\bullet} \qquad (6)$$

first halflife of 2.0 ms. The underlying process may well be dimerization of the adduct radical, a reaction suggested to occur also on the basis of a recent ESR study.[11] Depending on the wavelength some permanent absorption remains after this decay, which is attributed to the presumed $(C_{60}{-}Me)_2$ dimer, and to a contribution by $C_{60}{}^{\bullet -}$ radical anions generated by reduction through the also present propan-2-ol radicals.

A bimolecular rate constant of $k = 4.6\ (\pm 2) \times 10^8\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ has been evaluated from the build-up of the transient absorption at 370 nm and accordingly may be attributed to the addition reaction [eqn. (6)]. It must be recognized though that the reduction reaction [eqn. (1)] occurs at about the same rate and certainly superimposes on the observable reaction kinetics.

Qualitatively similar observations supporting this assignment have been made with MeBr and CF_3Br as electron scavengers.[24]

With respect to the rate constant our result agrees with that published for a presumed addition of ${}^{\bullet}CCl_3$ to C_{60} in irradiated CCl_4 solution.[12] The spectrum of the suggested $(C_{60}{-}CCl_3)^{\bullet}$ adduct radical differs, however, significantly from that of our methyl radical adduct, $(C_{60}{-}Me)^{\bullet}$, showing maxima at 440 nm[12] and 370 nm, respectively. furthermore, no information has been provided in the CCl_4 study[12] on a possible decay of the presumed adduct radical in the millisecond time range.

In conclusion, redox and free radical reactions with C_{60} can successfully be studied by radiation chemical methods, and in particular by the time-resolved technique of pulse radiolysis.

The authors thank Professor C. S. Foote who kindly provided us with a sample of fullerene for early test experiments, and with a set of extinction coefficients of C_{60} in solution. We are also indebted to Professor Ch. Schöneich for some experimental help and valuable discussions during the early stages of this work.

Received, 28th August 1992; Com. 2/04635K

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