Selective two-electron reduction of C_{60} by 10-methyl-9,10-dihydroacridine *via* photoinduced electron transfer

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The selective two-electron reduction of C_{60} to 1,2-dihydro[60]fullerene is attained *via* photoinduced electron transfer from 10-methyl-9,10-dihydroacridine to the triplet excited state of C_{60} in the presence of trifluoroacetic acid in benzonitrile under irradiation of visible light.

The preparation of dihydro[60]fullerene ($C_{60}H_2$) has recently attracted considerable interest, since it is the simplest C_{60} hydrocarbon derivative.[1,2] The reduction of C_{60} has so far been achieved by the use of strong reductants such as BH_3, which yield not only $C_{60}H_2$ but also polyhydride mixtures ($C_{60}H_{2n}$, $n = 2$ and 3).[1,2] Thus, the use of relatively mild reductants to achieve the selective reduction of C_{60} to $C_{60}H_2$ is desirable. However, C_{60} in the ground state has proved extremely difficult to reduce with mild reductants. We report herein the selective two-electron reduction of C_{60} by a mild hydride donor, 10-methyl-9,10-dihydroacridine ($AcrH_2$), *via* photoinduced electron transfer from $AcrH_2$ to the triplet excited state of C_{60} ($^3C_{60}*$) in the presence of trifluoroacetic acid in benzonitrile (PhCN) to yield 1,2-$C_{60}H_2$ selectively [eqn. (1)].

$$(1)$$
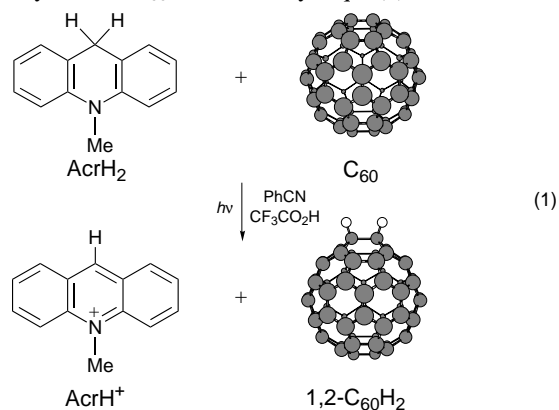
The hydride donor $AcrH_2$ and its deuteriated analogue 10-methyl[9,9-$^2H_2$]acridine ($AcrD_2$) were prepared as previously described.[3] To a solution of C_{60} (10.1 mg, 0.014 mmol) in deaerated PhCN (50 ml) was added $AcrH_2$ (2.7 mg, 0.014 mmol) and CF_3CO_2H (0.014 mmol), and the solution was irradiated with a Xe lamp equipped with a UV-cut filter ($\lambda < 540$ nm) for 30 min. After evaporation of PhCN under reduced pressure, the residue was separated by washing with MeCN and centrifuged to give 1,2-$C_{60}H_2$ exclusively in 70% yield.† In the dark, however, no reaction occurred even at high temperatures (*e.g.* 373 K). No appreciable amount of polyadducts was obtained even after a prolonged irradiation time under the present experimental conditions. The ^1H NMR signal at δ 5.91 (s, 2H) of 1,2-$C_{60}H_2$ (400 MHz, in C_6D_6) agrees well with that reported previously.[1] The visible spectrum exhibits an absorption maximum at $\lambda_{max} = 434$ nm, which is known to be characteristic of a 1,2-monoadduct resulting from 1,2-addition to a 6–6 bond.[2] Theoretical investigation also indicates that 1,2-$C_{60}H_2$ is the most stable form among 23 different regioisomers.[4]

When the photoreduction of C_{60} by $AcrH_2$ is carried out in the presence of NaI, the reaction is strongly inhibited. Since NaI is a well-known triplet quencher,[5] the photoreduction of C_{60} probably proceeds *via* $^3C_{60}*$, which is quenched by NaI to retard the photoreduction. In fact, the lifetime of the transient $^3C_{60}*$ triplet–triplet (T–T) absorption at $\lambda_{max} = 740$ nm is significantly reduced by the presence of $AcrH_2$. The bimolecular quenching rate constant (k_q) of $^3C_{60}*$ by $AcrH_2$ was determined to be 4.3×10^9 dm^3 mol^{-1} s^{-1} from the decay kinetics of transient T–T absorption at 740 nm following excitation at 355 nm. The quantum yields (Φ) were also determined from an increase in absorbance due to 1,2-$C_{60}H_2$ by using a ferrioxalate actinometer[6] under irradiation of monochromatized light of $\lambda = 546$ nm. The Φ value for the photoreduction of C_{60} by $AcrH_2$ in PhCN increases with an increase in the concentration of $AcrH_2$ to reach a limiting value (Φ_∞) as shown in Fig. 1. From the dependence of Φ on $[AcrH_2]$ is obtained the quenching constant K_{obs} ($= k_{obs}\tau_T$), which is converted to the rate constant (k_{obs}) for the reaction of $^3C_{60}*$ with $AcrH_2$ (5.0×10^9 dm^3 mol^{-1} s^{-1}) by using τ_T for $^3C_{60}*$ (32 µs) in PhCN.[7] The k_{obs} value agrees with a k_q value (4.3×10^9 dm^3 mol^{-1} s^{-1}) determined independently (*vide supra*). Such an agreement confirms that the photoreduction of C_{60} proceeds *via* the triplet excited state.
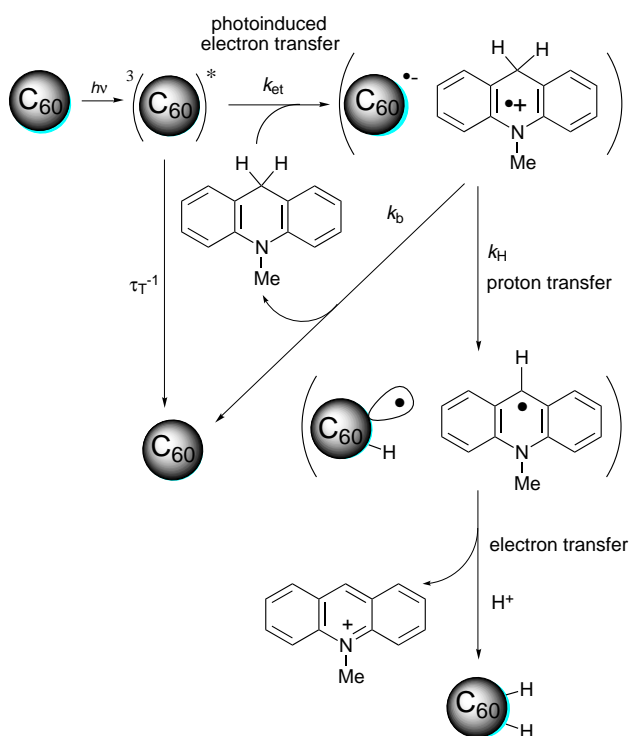
The free energy change of the photoinduced electron transfer from $AcrH_2$ to $^3C_{60}*$ is negative ($\Delta G^0_{et} = -32$ kJ mol^{-1}) judging from the fact that the one-electron oxidation potential of $AcrH_2$ (E^0_{ox} *vs.* SCE = 0.81 V)[8] is lower than the one-electron reduction potential of $^3C_{60}*$ (E^0_{red} *vs.* SCE = 1.14 V).[9] In such
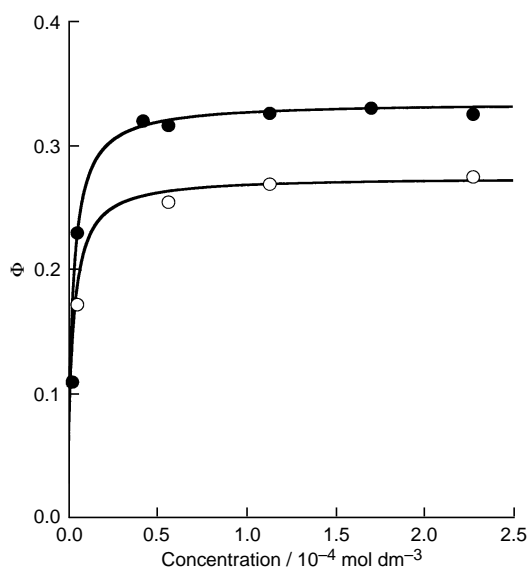
Fig. 1 Dependence of the quantum yield on the concentration of $AcrH_2$ and $AcrD_2$ for the photoreduction of C_{60} (2.8×10^{-4} mol dm^{-3}) by ● $AcrH_2$ and ○ $AcrD_2$ in the presence of CF_3CO_2H (5.6×10^{-4} mol dm^{-3}) in PhCN at 298K.

a case the electron transfer rate constant (k_{et}) may reach the diffusion-limited value in PhCN (5.6×10^9 dm^3 mol^{-1} s^{-1}),[9] which agrees with both the k_{obs} and k_q values (*vide supra*). Thus, the photoreduction of C$_{60}$ by AcrH$_2$ may proceed *via* photoinduced electron transfer from AcrH$_2$ to ^{3}C$_{60}$* (k_{et}) as shown in Scheme 1. The photoinduced electron transfer gives the radical ion pair in competition with the decay to the ground state ($k_T = \tau_T^{-1}$). Since AcrH$_2$·$^+$ is known to be a very strong acid,[8] proton transfer from AcrH$_2$·$^+$ to C$_{60}$·$^-$ (k_H) may occur in the radical ion pair in competition with the back electron transfer to the reactant pair (k_b), to give C$_{60}$H·, which is converted to 1,2-C$_{60}$H$_2$ by fast electron transfer from AcrH· in the presence of CF$_3$CO$_2$H. By applying the steady-state approximation to the reactive species, ^{3}C$_{60}$* and the radical ion pair in Scheme 1, the dependence of Φ on [AcrH$_2$] can be derived as given by eqn. (2), which agrees with the observed dependence of Φ on

$$\Phi = (k_H/(k_H + k_b))k_{et}\tau_T[\text{AcrH}_2]/(1 + k_{et}\tau_T[\text{AcrH}_2]) \quad (1)$$

[AcrH$_2$] in Fig. 1. The limiting quantum yield Φ_∞ corresponds to $k_H/(k_H + k_b)$. Thus, the Φ_∞ value being smaller than unity (0.33) may be ascribed to the competition of the proton transfer process (k_H) with the back electron transfer process (k_b). The existence of a protonation step following the photoinduced electron transfer is confirmed by the observed deuterium isotope effect in the limiting quantum yield ($\Phi_\infty{}_H/\Phi_\infty{}_D = 1.2$ in Fig. 1) when AcrH$_2$ is replaced by the deuteriated compound (AcrD$_2$). In contrast, no kinetic isotope effect was observed for the rate constant of electron transfer.

Alternatively, C$_{60}$·$^-$ produced in the initial photoinduced electron transfer from AcrH$_2$ to C$_{60}$ could be protonated by the acid, and hydrogen transfer from AcrH$_2$·$^+$ to C$_{60}$H· gives the final products. However, no increase in the quantum yield was observed with an increase in the amount of CF$_3$CO$_2$H. In addition, the reduction potential of C$_{60}$ was not affected by the presence of CF$_3$CO$_2$H in PhCN, as previously observed.[10] Thus, the protonation of C$_{60}$·$^+$ probably occurs *via* AcrH$_2$·$^+$ in the radical ion pair rather than *via* CF$_3$CO$_2$H (Scheme 1).

Footnote

† The yield was determined by HPLC equipped with an analytical 'Buckyclutcher I' column (Regis, Morton Grove, IL). A hexane–toluene mixture was used as eluent with a flow rate of 2 ml min^{-1}. The product was monitored at 434 nm with a UV-VIS detector.

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Scheme 1