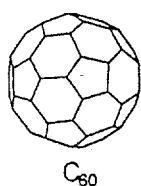


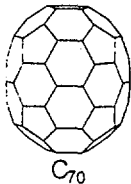
PHOTOINDUCED ELECTRON TRANSFER TO FULLERENE C₇₀. (AN *IN SITU* EPR STUDY)

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The extensive investigations of the unique photochemical and photophysical properties of fullerenes were carried out in the past years [1]. The electron transfer to fullerene C₆₀ was intensively studied by EPR [2], UV/Vis/Near-IR spectroscopy [3] and laser flash techniques [4]. In our previous EPR and Near-IR studies we observed the formation of C₆₀ anion-radicals induced by the electron transfer from the photoactivated TiO₂ particle [5], or by the quenching photoexcited triplet state of fullerene C₆₀ [6] and its derivatives [7]. On the other hand, there is only limited information on the generation of anion-radicals of C₇₀ and their characterization [8].



The photoexcitation of fullerene C₇₀ by monochromatic light ($\lambda=546$ nm) in the presence of electron donating substrate 3,3',5,5'-tetramethyl-benzidine (TMB) resulted in the charge-transfer, quenching the fullerene triplet state and forming the corresponding C₇₀ anion-radicals. Analogously to the photoreduction of C₆₀, two EPR signals were observed upon *in situ* irradiation in the cavity of EPR spectrometer. EPR singlet A characterized by g-value, $g_A=2.0009$ and peak-to-peak line-width, $pp_A=0.013$ mT was assigned to the C₇₀ mono-anion. Signal B ($g_B=2.0011$; $pp_B=0.011$ mT) was tentatively attributed to the C₇₀ di-anion or to the associated forms of mono-anion (Fig.1).

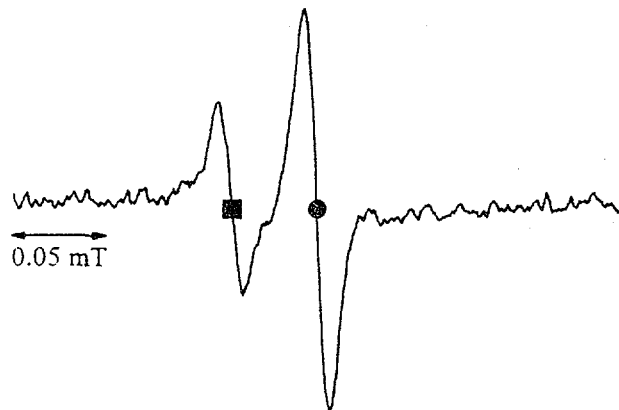


Figure 1

EPR spectrum observed during continuous irradiation of C₇₀ and TMB in DCIB/acetonitrile = 4:3 (v/v) solvent mixture.
 $[C_{70}] = 4.08 \times 10^{-4} \text{ mol dm}^{-3}$
 $[TMB] = 4.5 \times 10^{-3} \text{ mol dm}^{-3}$
 ●...A, $g_A = 2.0009$, $pp_A = 0.013$ mT;
 ■...B, $g_B = 2.0011$, $pp_B = 0.011$ mT.

The stabilization of photogenerated anion-radicals is significantly dependent on solvent polarity. The shortest lifetime of radicals was found in 1,2-dichlorobenzene (DCIB) (Fig.2), and it increased considerably upon addition of tetrabutylammonium hexafluoro-phosphate salt or acetonitrile to the C₇₀ DCIB solution, or if DCIB was replaced by benzonitrile. The concentration of radicals A and B formed during irradiation sensitively reflected the composition of solution irradiated (solvent, C₇₀ and TMB concentrations) and irradiation period.

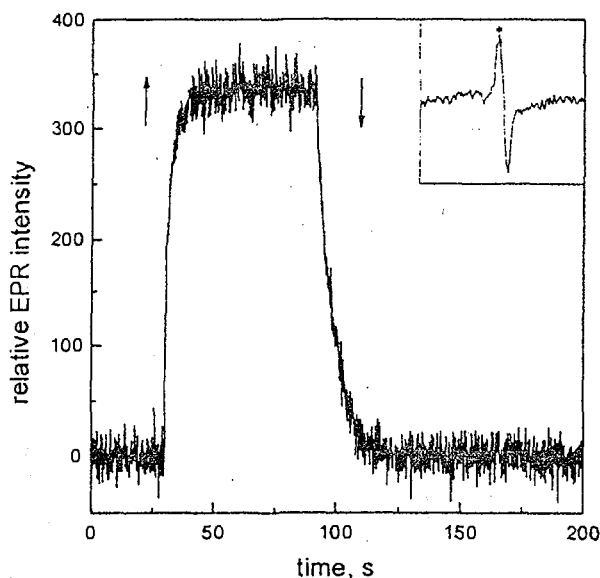


Figure 2

The time dependence of the relative intensity of EPR signal A (*), monitored during irradiation (↑) and after irradiation stopping (↓) in the DCIB solution of C₇₀ and TMB ([C₇₀]=8.2 × 10⁻⁴ mol dm⁻³, [TMB]=0.001 mol dm⁻³). Inset: EPR spectrum observed during irradiation.

Radical A was generated also in the solid state, irradiating frozen C₇₀ and TMB solution in DCIB at temperature of 200 K. Lowering the temperature, the EPR line A became broader and asymmetric. At 110 K the observed EPR spectrum can be simulated by an axially symmetric g-matrix with $g_{||}-g_{\perp}=0.00165$.

Acknowledgements

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