0.69 ± 0.06 for both the investigated wavelengths. Our quantitative data were explained on the grounds of a reaction mechanism involving an intermediate $[Fe(C_2O_4)_2(C_2O_4 \cdot)]^{3-}$ which we detected by flash photolysis. This intermediate decayed by a first-order process with a rate constant $k = (1.46 \pm 0.08) \times 10^3 \text{ s}^{-1}$ according to the structure of a $C_2O_4^-$ monodentate radical coordinated to an Fe(II) oxalate complex.

We also estimated a value of 0.54 for the ratio of the rate constant for the ligand-to-metal charge transfer process to the rate constant for the internal conversion process.

Detection of radical ions in solution: the possible intermediacy of a Rydberg state

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Transient spectra obtained from flash photolysis of benzyl-1-pyrenoate (M) in various solvents with high ionization potentials showed the formation of the triplet state ($\lambda = 425$ nm) and of the radical anion ($\lambda = 510$ nm). The following mechanism is proposed:

$$M \xrightarrow{h\nu}{}^{1}M^{*} \xrightarrow{k_{isc}}{}^{3}M^{*} \xrightarrow{h\nu'}{}^{(M^{+} \cdot e^{-})} \xrightarrow{+M}{}^{K_{4}} M^{\cdot +} + M^{\cdot -} \xrightarrow{k_{5}}{}^{K_{5}}$$

The six rate constants obtained by fitting the transient decays are $k_1 = 1.6 \times 10^2 \text{ s}^{-1}$, $k_2 = 1.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_3 = 2.3 \times 10^3 \text{ s}^{-1}$, $k_4 = 1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $k_5 = 1.2 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $k_6[Q] = 3.5 \times 10^2 \text{ s}^{-1}$. Their orders of magnitude are those expected from the mechanism proposed which is also consistent with the following experimental data: (a) a lack of correlation with the ionization potentials and efficiency of $M \cdot \overline{}$ formation; (b) the fact that oxygen does not quench the $M \cdot \overline{}$ formation; (c) the dependence of the quantum yield of the $M \cdot \overline{}$ on the square of the light intensity; (d) the fact that the kinetics of formation and disappearance of either transient at 425 and 510 nm excludes an electron transfer process after triplet-triplet annihilation; (e) correlation between the molar polarizability and the quantum yield of the $M \cdot \overline{}$. The hypothesis of a Rydberg state as an intermediate is discussed on the basis of the kinetic evidence and ionization energies involved.