Metal-to-ligand Charge Transfer Photochemistry: Potential Energy Curves for the Homolysis of the Model System HMn(CO$_3$)(α-diimine)

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The presence of a reactive ^{3}LLCT (σ → π*) excited state interacting with the low-lying metal-to-ligand charge transfer (MLCT) states and leading to the primary products H + Mn(CO)$_3$(α-diimine) in their ground state is responsible for the formation of the radical species in this family of molecules; the quantum yield and the time-scale of the homolysis will depend on factors capable of modifying the barrier energy height, namely the nature of the radical species to be produced, the metal centre, the π-acceptor ligand and the experimental conditions.

Until recently MLCT states were assumed to be mostly unreactive and their long lifetimes made them suitable for spectroscopic analysis.[1–5] However, according to a number of experiments reported for a family of α-diimine mono- and dinuclear transition metal carbonyls,[6–14] it seems that these molecules may either behave like transition metal complexes without low-lying MLCT states, undergoing ligand dissociation or radical formation upon irradiation, or manifest the photophysics of MLCT complexes. This duality of behaviour may be used to promote different applications like energy and electron-transfer processes or formation of reactive intermediates used in substitution reactions and catalytic processes. A fundamental question concerns the function of the MLCT states in the observed photochemistry of this class of molecules which depends strongly on the metal centre, the ligand π-acceptor and the other ligands. The relative positions in the electronic spectra of the photodissociative states correspondign to d → d, d → σ*, σ → σ*, σ → π* excitations with respect to the MLCT states is probably the key to the photochemical behaviour of this family of molecules. One way of obtaining insights into the nature of the photoexcited states involved in the photochemistry of these molecules is to calculate the excitation energies of the lowest electronic states and the corresponding potential energy curves for the observed primary reactions (homolysis of the metal–R or metal–metal bond *vs.* CO loss).[15–18] This approach constitutes the first step of a more complete study based on the calculation of the potential energy surfaces, followed by an investigation of the photodissociation dynamics.[19–22]

In the present work, the homolysis of the metal–hydrogen bond of the model system HMn(CO)$_3$(α-diimine) [eqn. (1)]

$$\mathrm{HMn(CO)_3(\alpha\text{-diimine})} \xrightarrow{h\nu} \mathrm{H + Mn(CO)_3(\alpha\text{-diimine})} \quad (1)$$

has been studied through contracted configuration interaction (CCI) calculations based on complete active space self-consistent field (CASSCF) wavefunctions. The potential energy curves that connect the singlet electronic ground state and the three lowest triplet excited states of the reactant to the singlet/triplet diradical ground state and the lowest triplet excited states of the primary products H + Mn(CO)$_3$(α-diimine) have been calculated under C_s constraints with a basis set that is at least of double-ζ quality. For each state a multi-reference CCI calculation that correlates the 3d electrons and the two electrons of the Mn–H bond was performed, based on a CASSCF wavefunction with eight electrons in ten active orbitals ($3d_{yz}$, $3d_{x^2-y^2}$, $3d_{xz}$, $\sigma_{\mathrm{Mn-H}}$, $\sigma^*_{\mathrm{Mn-H}}$, $3d_{xy}$, $4d_{yz}$, $4d_{x^2-y^2}$, $4d_{xz}$, π*) optimized for the electronic configuration of interest. The calculations were carried out for the model system HMn(CO)$_3$(α-diimine) (α-diimine = 1,4-diazabuta-1,3-diene) with the conformation shown in Fig. 1 in C_s symmetry.

The lowest states, accessible through the spin- and symmetry-allowed $^1A' \rightarrow {}^1A'$ and $^1A' \rightarrow {}^1A''$ transitions range between 17110 and 22280 cm^{-1} and correspond to d → π* excitations,[23] in excellent agreement with the main feature of the UV–VIS absorption spectra obtained, namely a large and very intense band at 500 nm assigned to MLCT states. The next state accessible through an allowed transition is the ^{1}LLCT (σ → π*) excited state. In this preliminary study, the calculation of the potential energy curves (PECs) is restricted to three low-lying $^3A'$ excited states for two reasons: (i) the nature of the electronic structure of the primary products, namely a $^{1,3}A'$ diradical, and (ii) the existence of experimental emission spectra from the low-lying triplet states. The potential energy curves for the a$^1A'$ electronic ground state and the three lowest $^3A'$ excited states of HMn(CO)$_3$(α-diimine), namely the a$^3A'$ and b$^3A'$ MLCT states corresponding to $d_{xz} \rightarrow \pi^*$ and $d_{x^2-y^2} \rightarrow \pi^*$ excitations, respectively, and the c$^3A'$ state corresponding to the σ → π* excitation, calculated along the Mn–H bond homolysis reaction path under C_s symmetry constraints, are shown in Fig. 2.

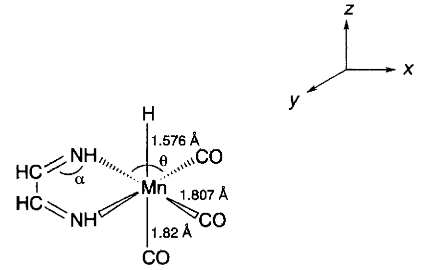

Fig. 1 Conformation of the model system HMn(CO)$_3$(α-diimine)

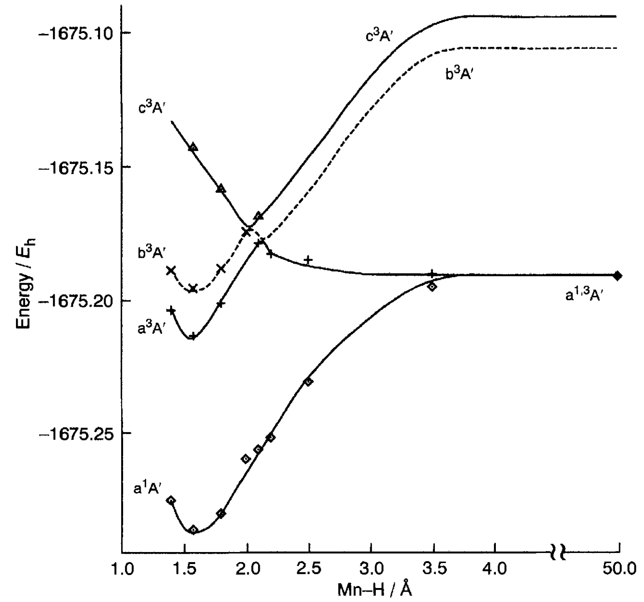

Fig. 2 CASSCF/CCI potential energy cruves for the homolysis of the Mn–H bond in HMn(CO)$_3$(α-diimine) as a function of the Mn–H bond distance (the points correspond to the *ab initio* values)

Reaction (1) is calculated to be endothermic by 60.0 kcal mol^{-1} (1 cal = 4.184 J). The character of the a^1A' PEC is modified around 3.5 Å, owing to its interaction with the $^1A'$ dissociative PEC (not represented here) corresponding to the $\sigma \rightarrow \pi^*$ excitation. The lowest a^3A' and b^3A' potential energy curves, corresponding to MLCT states, are quasi-bound in the vicinity of the equilibrium geometry, in agreement with the absorption and emission spectra reported for this family of molecules. The a^3A' PEC corresponds in its dissociative part to the $\sigma \rightarrow \pi^*$ excitation and leads to the primary products H + $Mn(CO)_3$(α-diimine) in their $a^{1,3}A'$ ground state. The b^3A' PEC avoids two crossings, the first one with the a^3A' PEC giving an energy barrier around 2.11 Å of the order of 20.0 kcal mol^{-1}, the second one was the upper c^3A' PEC around 2.02 Å. The second avoided crossing generates an energy barrier of the order of 14.0 kcal mol^{-1} on the b^3A' PEC. The two upper b^3A' and c^3A' and c^3A' PECs become totally attractive beyond 2.1 Å.

From the shapes of the potential energy curves obtained in this way, it appears that the interaction between the two lowest $^3A'(d \rightarrow \pi^*)$ MLCT excited states and the $^3A'$ $(\sigma \rightarrow \pi^*)$ LLCT dissociative state, which correlates with the primary products H + $Mn(CO)_3$(α-diimine) in their ground states, plays a key role in the photochemical behaviour of this family of molecules. Indeed, two potential energy barriers, due to avoided crossings between the two lowest $^3A'$ MLCT states and the $^3A'(\sigma \rightarrow \pi^*)$ dissociative state occur at Mn–H distances of 2.02 and 2.11 Å. It is proposed that excitation of $HMn(CO)_3$(α-diimine) at high energy (around 330 nm) will bring the system into one of the singlet states corresponding to $d \rightarrow d$ or $\sigma \rightarrow \pi^*$ excitations (calculated between 27800 and 34850 cm^{-1}), whereas low energy excitation (around 500 nm) will bring the molecule into the lowest ^{1}MLCT states (calculated between 17110 and 22280 cm^{-1}). From the highest singlet states, after fast intersystem crossing to the $^3A'$ $(\sigma \rightarrow \pi^*)$, the system will reach the lowest a^3A' dissociative potential energy curve through internal conversions at 2.02 and 2.11 Å and evolve to the primary products H + $Mn(CO)_3$(α-diimine) in their ground states. From the lowest ^{1}MLCT states, after fast intersystem crossing to the corresponding ^{3}MLCT states, the system may either become trapped in the potential well of these long-lived excited states and provide emission spectra or be able to overcome the energy barriers yielding a fraction of the primary products H + $Mn(CO)_3$(α-diimine) in their ground states. This fraction, depending on the barrier energy height, could be determined by photodissociation dynamics simulation.[19–22,25]

The potential energy curves obtained for the homolysis of the metal–hydrogen bond in the simple model system $HMn(CO)_3$(α-diimine) point to the complexity and richness of the photochemistry of transition metal complexes with low-lying MLCT states. This work represents the first theoretical evidence of the participation of the low-lying MLCT states in the photodissociation mechanism of these molecules. The presence of a ^{3}LLCT $(\sigma \rightarrow \pi^*)$ photoactive excited state confirms the conclusions of recent experiments reported for this class of compounds,[26] namely a fast homolysis observed for Mn(benzyl)$(CO)_3$(Pr^i-dab) (dab = 1,4-diazabuta-1,3-diene) (τ < 10 ns) without any long-lived excited state. Similar behaviour is observed when Mn is replaced by Re. The interaction between the MLCT states and the low-lying LLCT $(\sigma \rightarrow \pi^*)$ dissociative excited state for the metal–hydrogen bond breaking and probably for the other primary reactions leading to radical species (metal–alkyl or metal–metal bond homolysis) is the key to the mechanism. The quantum yield and the timescale of the homolysis will depend on the factors (wavelength of irradiation, nature of the radical species to be produced, metal centre and π-acceptor ligand) governing the facility for the system to overcome the energy barrier occurring at the avoided crossing points between this photoactive excited state and one of the lowest MLCT states. For instance, if the homolysis reaction of M(benzyl)$(CO)_3$(Pr^i-dab) (M = Mn, Re) is characterized by a quantum yield close to one, the analogous methyl M(methyl)$(CO)_3$(Pr^i-dab) do not (M = Mn) or hardly (M = Re) show homolysis upon VIS excitation into the MLCT band, indicating the presence of a high energy barrier. A detailed analysis of the excitation energies and of the PECs corresponding to the ground and excited states of $HMn(CO)_3$(α-diimine) calculated for the metal–hydrogen and metal–carbonyl bond elongations will be published elsewhere.[24]

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