Photochemistry of organometallics: potential energy surfaces and reaction mechanisms

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Abstract - Configuration interaction calculations, based on Complete Active Space SCF wavefunctions, are reported for the lowest excited states of Fe(CO)$_3$, HMn(CO)$_3$, and HCo(CO)$_3$. Potential energy curves have been computed at the same level of accuracy for the photodissociation of HCo(CO)$_3$. The mechanism of the photochemical reactions of these organometallics is discussed. The cis stereospecificity of the photosubstitution of d$^6$ metal carbonyls is explained on the basis of state correlation diagrams.

INTRODUCTION

There is an extensive photochemistry of organometallics (ref. 1). As noted in a recent review, "one unfortunate characteristic of much of organometallic photochemistry is a relative absence of detailed mechanistic information. Without such information the systematic and rationally planned use of photochemical techniques and the exploitation of photochemical intermediates are left largely to chance" (ref. 2). Current understanding (ref. 1) has been based on molecular orbital diagrams coupled with an analysis in terms of bonding and antibonding character, with the assumption that exciting an electron from a bonding to the corresponding antibonding orbital should result in photodissociation. This approach fails for instance to interpret the photosubstitution of CO in iron tricarbonyl di- and tetrazabutadiene complexes, since the calculations do not show any change in metal-CO bonding in the lowest excited states (ref. 3). It is unable to explain the occurrence of competitive photochemical reactions at a given wavelength, such as the simultaneous photolytic cleavage of the metal-hydrogen and photochemical loss of a carbonyl ligand reported for HCo(CO)$_3$, or the concurrent cleavage of the metal-metal bond and loss of a carbonyl ligand found in the photochemistry of Mn$_2$(CO)$_6$ (ref.2 and 4).

A deep understanding of photochemical reactions requires a knowledge of the potential energy surfaces (PES) which connect the reactants to the primary photochemical products. Whenever potential energy surfaces are not available, one may rely on their qualitative counterparts, the state correlation diagrams (Ref. 5). We have been engaged, for the last few years, in the derivation of state correlation diagrams and in the calculation of potential energy curves for representative photochemical reactions of organometallics (Ref. 6-12). We present here a survey of the methodology and of the results.

METHODOLOGY

The method used should reproduce correctly the sequence and energetics of electronic states of the reactant and products. For this reason the SCF method is generally not appropriate for the calculation of PES, since it frequently leads to errors of 1 eV or more in the calculated excitation energies (Ref. 13). Configuration interaction (CI) based on SCF reference wavefunctions gives results which are qualitatively correct in general, however accurate results may require very long CI expansions (ref. 9). The CASSCF (Complete Active Space SCF) method (Ref. 14) has been used to obtain reference wavefunctions and orbitals for the calculation of excited states of Fe(CO)$_3$ and HMn(CO)$_3$, and of the PES for HCo(CO)$_3$. These CASSCF calculations were followed by contracted CI (CCI) calculations (ref. 15).

The rigorous way to calculate excitation energies and potential energy surfaces consists of carrying out for each electronic state a CASSCF calculation followed by a contracted CI calculation (ref. 16). However this method becomes too expensive for the studies reported here. The approach which we have used consists of performing a CASSCF calculation for a particular state and using this CASSCF reference wavefunction for the CCI calculations of all the states of interest (Ref. 12). The choice of this particular state was dictated by the following considerations. The ground state is not the best candidate, since the CCI calculations would be biased in favour of this state and would
lead to overestimated excitation energies. Whenever possible, we have selected a state with an occupation number close to one for the orbitals which are empty in the ground state but populated in the low-lying excited states. Details of these CASSCF calculations are given in Table 1. For Fe(CO)$_5$, the occurrence of symmetry breaking solutions forced us to rely on a CASSCF wavefunction optimized for the ground state.

**TABLE 1. The CASSCF calculations**

<table>
<thead>
<tr>
<th>State</th>
<th>Principal Configuration</th>
<th>Active Space in active space</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)$_6$</td>
<td>$^7A_g$</td>
<td>$t^3_2e^2g^1_2g^1$</td>
</tr>
<tr>
<td>HMMn(CO)$_6$</td>
<td>$^5A_2$</td>
<td>$d^2_2g^1c^1d^1_2g^1$</td>
</tr>
<tr>
<td>Fe(CO)$_5$</td>
<td>$^1A_1$</td>
<td>$d^3_2d^1_2d^1$</td>
</tr>
<tr>
<td>HCo(CO)$_4$</td>
<td>$^3A_1$</td>
<td>$d^3_2d^1_2d^1$</td>
</tr>
</tbody>
</table>

*a* $\sigma$ and $\sigma^*$ denote the m.o.'s which are bonding and antibonding with respect to the metal-hydrogen bond.

For each electronic state, two CCI calculations were performed. The first one has only one reference configuration while the second one is a multireference calculation. The reference configurations of the second one are the configurations with a coefficient greater than a given threshold (usually between 0.08 and 0.065) in the wavefunction of the first calculation. The number of reference configurations selected in this way was between 2 and 10. The number of electrons correlated was 6 in Cr(CO)$_6$, 8 in HMMn(CO)$_6$ and Fe(CO)$_5$ (namely the 3d electrons and the 2 electrons of the Mn-H bond in HMMn(CO)$_6$) and 6 in HCo(CO)$_4$ (the 3d electrons and the 2 electrons of the Co-H bond). The calculations included single and double excitations to all virtual orbitals except the counterparts of the carbonyl Is and of the metal Is, 2s and 2p orbitals. The number of configurations ranged from 36000 to 317000 for HMMn(CO)$_6$ and from 183000 to 509000 for HCo(CO)$_4$, but this number was reduced to at most a few thousands by the contraction.

The following gaussian basis sets were used: for the transition metal a (15,11,6) set contracted to [9,6,3] (ref. 17), for the first row atoms a (10,6) set contracted to [4,2] (ref. 18) and for hydrogen a (6,1) set contracted to [3,1] (ref. 19). This basis set is triple-zeta for the Is shell of hydrogen and for the 3d and 4s shells of the transition atoms, otherwise it is double-zeta.

The calculations for Cr(CO)$_6$, HMMn(CO)$_6$, Fe(CO)$_5$ and HCo(CO)$_4$ were performed for the experimental geometry of these molecules (ref. 20-22). For the calculation of the potential energy curves of HCo(CO)$_4$, we have assumed that $C_2v$ symmetry was retained along the reaction path since both Co(CO)$_5$ and HCo(CO)$_4$ have been found to have $C_2v$ symmetry in their ground state (ref. 10 and 23).

The integral and SCF calculations were carried out either with the system of programs ASTERIX (ref. 24) or with the system of programs ARGOS (ref. 25). The CASSCF and CCI calculations were performed with the system SWEDEN (ref. 26).

**CALCULATION OF EXCITED STATES**

One major difficulty in the calculations of excited states is due to the fact that organometallics are characterized by the occurrence of a large number of excited states within a relatively narrow energy region. For instance 18 excited states were located between 33000 and 51000 cm$^{-1}$ for Fe(CO)$_5$ (ref. 9). Another difficulty arises when one wants to compare the calculated excitation energies to experimental values, since the electronic spectra of organometallics are poorly resolved in general (certainly as a consequence of this high density of states). These electronic spectra show usually a broad band (corresponding generally to a charge transfer transition) with one or two shoulders (see for instance ref. 1, 27 and 28). Since our interest centers mostly on the ligand field (LF), $d + \sigma^*$ and $\sigma + \sigma^*$ excitations which turn out to be responsible of the photochemical reactions studied here, we have not in general calculated the many metal-to-ligand charge-transfer (MLCT) excited states corresponding to the $d + \sigma^*$ excitations or the Rydberg type excited states (corresponding to the $3d + 4d$, 5s, 5p excitations). We shall review briefly the main results.
Fe(CO)₅
The LF excited states ¹E' and ¹E" are calculated respectively at 33400 and 34100 cm⁻¹ (ref. 12). Since these excitation energies were obtained with a CASSCF reference wavefunction optimized for the ground state, they are probably overestimated by about 5000 cm⁻¹ as judged from the results obtained for the LF states of HMn(CO)₅ with different reference wavefunctions (Table 2). This would put the LF state ¹E' at about 28600-29000 cm⁻¹. This is in good agreement with the experimental spectrum which shows a very weak absorption in the region of 28600 cm⁻¹ (ref. 29).

HMn(CO)₅
The calculated excitation energies are shown in Table 2. The 3A₁ σ + σ* excitation is computed at 46900 cm⁻¹. One 3d⁺xy + 4d⁻xy transition, calculated at 49000 cm⁻¹, may correspond to a Rydberg transition (although this 4d orbital is localized in the same region of space as the 3d orbitals), in good agreement with the fact that excitation to the 4d level starts at 47000 cm⁻¹ for the Mn atom (ref. 30). The experimental spectrum of HMn(CO)₅ in the gas phase shows one broad band around 46700 cm⁻¹ with two shoulders at 34500 and 51300 cm⁻¹, these three features having been assigned as MLCT transitions (ref. 28). According to the results of Table 2, the transition at 34500 cm⁻¹ should rather correspond to the LF excitations. This assignment is supported by the low value of the intensity in the experimental spectrum, a general feature of the LF transitions. The intense band at 46700 cm⁻¹ corresponds probably to several transitions such as the d⁺σ, 3d + 4d and MLCT transitions (the allowed transition ¹A₁ + ¹E corresponding to the d⁺σ excitation is computed at 42300 cm⁻¹).

TABLE 2. Calculated excitation energies (in cm⁻¹) for HMn(CO)₅

<table>
<thead>
<tr>
<th>State</th>
<th>One-electron excitation</th>
<th>Energy (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>³A₂</td>
<td>dₓᵧ + dₓ²₋ᵧ²</td>
<td>27600</td>
</tr>
<tr>
<td>³E</td>
<td>dᵧ + dₓ²₋ᵧ²</td>
<td>28200</td>
</tr>
<tr>
<td>³A₁</td>
<td>σ + σ*</td>
<td>46900</td>
</tr>
<tr>
<td>¹A₂</td>
<td>dₓᵧ + dₓ²₋ᵧ²</td>
<td>33300</td>
</tr>
<tr>
<td>¹E</td>
<td>dᵧ + σ*</td>
<td>33700</td>
</tr>
<tr>
<td>¹E</td>
<td>dᵧ + σ*</td>
<td>33700</td>
</tr>
<tr>
<td>¹B₂</td>
<td>dₓᵧ + σ⁺</td>
<td>53000</td>
</tr>
<tr>
<td>¹A₁</td>
<td>dₓᵧ + 4dₓᵧ</td>
<td>49000</td>
</tr>
<tr>
<td>¹A₂</td>
<td>dₓᵧ + π⁺</td>
<td>53600</td>
</tr>
<tr>
<td>¹A₁</td>
<td>σ + σ⁺</td>
<td>61800</td>
</tr>
</tbody>
</table>

a Symmetry allowed.
b From a CAS-SCF wavefunction optimized for the ground state.

HCo(CO)₄
A ²A₁ state corresponding to the σ + σ* excitation is computed at 34600 cm⁻¹. The ³E and ¹E states corresponding to the dₓᵧ + σ* excitation are calculated at 25900 and 36000 cm⁻¹ respectively. The absorption spectrum of HCo(CO)₄ shows an intense band at 44000 cm⁻¹ corresponding certainly to a CT transition (Ref. 4), with the weaker dₓᵧ + σ* transition probably buried under it.

MECHANISM OF PHOTOCHEMICAL REACTIONS

Photodissociation of Fe(CO)₅
The mechanism which we have proposed for the primary step of the photodissociation of Fe(CO)₅

\[
\text{Fe(CO)}₅ + h\nu \rightarrow \text{Fe(CO)}₄ + \text{CO}
\]
is based on state correlation diagrams and potential energy curves (ref. 6 and 9) which show that a single potential energy surface connects, without any barrier, the LF state \( \Sigma_{E} \) of \( \text{Fe(CO)}_5 \) to the ground state \( \Sigma_{B_2} \) of the products \( \text{Fe(CO)}_4 + \text{CO} \). This mechanism is represented in Fig. 1. Excitation to the LF state \( \Sigma_{E} \) is followed by intersystem crossing to the state \( \Sigma_{E} \). From there the molecule dissociates to the products of the reaction along the \( \Sigma_{B_2} \) potential energy surface (assuming that \( C_{4v} \) symmetry is retained along the reaction path). The conclusion that the LF excited state \( \Sigma_{E} \) correlates with the ground state of the products is independent of the assumptions made on the dissociating ligand (equatorial or axial) and on the symmetry retained along the reaction path (ref. 9). This mechanism has been used to interpret the results of laser photolysis experiments on \( \text{Fe(CO)}_5 \) in the gas phase (ref. 31).

![Fig. 1. The mechanism proposed for the photochemical dissociation of \( \text{Fe(CO)}_5 \).](image)

**Photochemistry of \( \text{HCo(CO)}_4 \)**

Irradiation of \( \text{HCo(CO)}_4 \) at 254 nm (39400 cm\(^{-1}\)) results in two photochemical reactions corresponding respectively to the loss of a carbonyl ligand and to the homolysis of the cobalt-hydrogen bond:

\[
\begin{align*}
\text{HCo(CO)}_4 & \xrightarrow{hv} \text{HCo(CO)}_3 + \text{CO} \\
\text{HCo(CO)}_4 & \xrightarrow{hv} \text{Co(CO)}_4 + \text{H}
\end{align*}
\]

Potential energy surfaces for the ground and excited states of \( \text{HCo(CO)}_4 \) (Fig. 2) have been inferred from the potential energy curves calculated for the loss of either the hydrogen or the axial carbonyl ligand (Ref. 23). These surfaces form the basis for a qualitative understanding of the photochemistry of \( \text{HCo(CO)}_4 \). We propose that irradiation at 254 nm brings the molecule into the \( \Sigma_{E} \) state (corresponding to the \( d_\pi^* - \sigma^* \) excitation and calculated at 36000 cm\(^{-1}\)), this being followed by intersystem crossing to the \( \Sigma_{A_1} \) \( \sigma^* - \pi^* \) state (calculated at 34600 cm\(^{-1}\)). From there the molecule may evolve along three different channels corresponding to:

i) the dissociation of the Co-H bond along the \( \Sigma_{A_1} \) curve, with formation of the products H and \( \text{Co(CO)}_4 \) in their ground state;

ii) the loss of a carbonyl ligand along the \( \Sigma_{A_1} \) curve, forming the products \( \text{CO} \) and \( \text{HCo(CO)}_3 \) in the excited state \( \Sigma_{A_1} \);

iii) the formation of the products \( \text{CO} \) and \( \text{HCo(CO)}_3 \) in the excited state \( \Sigma_{E} \) by crossing from the \( \Sigma_{A_1} \) to the \( \Sigma_{E} \) surface.

We predict that chemiluminescence should be observed for the photochemical decarbonylation in the gas phase (chemiluminescence has been predicted and observed for the photodecarbonylation of \( \text{Ni(CO)}_4 \), Ref. 9 and 32).

**Photochemistry of \( \text{HMn(CO)}_5 \)**

Depending on the wavelength, the photolysis of \( \text{HMn(CO)}_5 \) results either in carbonyl loss (at 229 nm or 43700 cm\(^{-1}\))

\[
\text{HMn(CO)}_5 \xrightarrow{hv} \text{HMn(CO)}_4 + \text{CO}
\]
or in hydrogen loss (at 193 nm or 51800 cm⁻¹)

\[ \text{HMn(CO)}_6 \xrightarrow{\text{hv}} \text{Mn(CO)}_6 + \text{H} \]

In the absence of potential energy surfaces for this system, any proposal for a mechanism should be viewed as tentative. The mechanism which we propose for hydrogen dissociation is based on a state correlation diagram (Ref. 7) and is similar to the one advanced for HCo(CO)₅. Irradiation at 51800 cm⁻¹ to a singlet state is followed by intersystem crossing to the \( ^3 \Sigma_g^+ \) state (calculated at 46900 cm⁻¹). From there the molecule dissociates along the \( ^1 \Sigma_g^+ \) potential energy curve to the products H and Mn(CO)₆ in their ground state. As to the photochemical loss of a carbonyl ligand observed at 43700 cm⁻¹, we tentatively propose that it results from excitation to the \( ^1 \Sigma_g^+ \) state (calculated at 42300 cm⁻¹) since the potential energy curve for the \( ^3 \Delta_d \rightarrow \sigma^* \) of HCo(CO)₅ is dissociative with respect to the loss of a carbonyl ligand (Fig. 2).

**Photosubstitution of d⁶ metal carbonyls**

Photosubstitution of monosubstituted d⁶ metal carbonyls M(CO)₅L may result in CO labilization and this reaction has been found to be highly stereospecific, yielding the cis isomer (references may be found in Ref. 11, see also Ref. 33):

\[ \text{hv M(CO)}_5\text{L} \xrightarrow{\text{hv}} \text{cis-M(CO)}_5\text{LL'} + \text{CO} \]

This reaction is the result of a photoelimination followed by a nucleophilic reaction:

\[ \text{M(CO)}_5\text{L} \xrightarrow{\text{hv}} \text{M(CO)}_5\text{L} + \text{CO} \]

\[ \text{M(CO)}_5\text{L} + \text{L'} \rightarrow \text{M(CO)}_6 \text{LL'} \]

SCF and CI calculations have been used to generate state correlation diagrams for the primary photoelimination (Ref. 11). Fig. 3 represents the state correlation diagram for the photoelimination of the axial carbonyl ligand from M(CO)₅L. On the basis of this diagram, we have proposed the following mechanism for the photosubstitution of the axial carbonyl ligand:

i) Excitation of M(CO)₅L into the \( ^1 \Sigma_d^+ \) state followed by elimination of the carbonyl ligand with the species M(CO)₅L formed in the excited state \( ^1 \Sigma_d^+ \) as a square pyramid with the ligand L apical;

ii) M(CO)₅L evolves along a Berry pseudorotation path first to a trigonal bipyramid in the \( ^1 \Sigma_g^+ \) state then to a square pyramid with L basal in the \( ^1 \Delta \) excited state;

iii) M(CO)₅L being trapped in the potential well corresponding to this excited state \( ^1 \Delta \) can evolve only through internal conversion to the ground state \( ^1 \Sigma \); iv) M(CO)₅L being trapped as a square pyramid with L basal in the potential well of the ground state \( ^1 \Sigma \) can only react with an incident nucleophile to give M(CO)₆LL' with the cis structure (Scheme 1).

**Scheme 1**

A similar analysis leads to the same conclusion for the photoelimination of an equatorial carbonyl ligand, namely that the product M(CO)₆LL' should be formed with the cis structure (Fig. 4). This analysis may also be extended (Ref. 11) to account for the stereospecificity observed in the photochemistry of M(CO)₅(L) where the ligand L occupies two cis coordination sites, as found in Mo(CO)₅(dppe) with the photosubstitution resulting in the sole production of fac-[Mo(CO)₅(dppe)L] (Ref. 34) or in the \((\pi^*\text{-diene})\text{Cr(CO)}_4\) complexes, with the photolysis resulting in the formation of fac-\((\pi^*\text{-diene})\text{Cr(CO)}_4\) (Ref. 35).
Photochemistry of peroxometalloporphyrin complexes

The photolysis of the peroxometalloporphyrin complexes Ti(O₂)(TPP) and Mo(O₂)(TPP) gives rise to evolution of O₂ in the 1A₁ excited state (Ref. 36):

$$\text{Ti(O}_2\text{)(TPP)} \rightarrow \text{TiP} + O_2$$

A state correlation diagram, based on SCF calculations for the reactant (Ref. 37) is shown in Fig. 5. The excited state 1A₁ of the reactant corresponds to the electronic configuration Ti(II)O₂ d⁸[π]* (where π⁰ and π¹ denote the π orbitals of dioxygen which are respectively symmetrical and antisymmetrical with respect to the plane defined by the Ti atom and the O₂ ligand) It correlates through an avoided crossing with the products TiP and O₂ in the 1A₂ state, providing a rationale for the experimental findings.

CONCLUSION

The calculation of potential energy surfaces (or potential energy curves) and the construction of state correlation diagrams has enabled us to get a better understanding of the mechanism of these photochemical reactions. The importance of intersystem crossing from a singlet state (reached through excitation of the reactant) to a triplet state (which connects to the ground state of the products) has become clear in the
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photochemistry of Fe(CO)₅ and HCo(CO)₅. It certainly represents a general mechanism for
the photochemical homolysis of a σ bond and could be extended to the photochemical
cleavage of the metal-carbon bond in RMn(CO)₅, of the metal-silicon bond in R₂SiCo(CO)₅,
and of the metal-metal bond in dinuclear complexes like Mn₂(CO)₁₀. The occurrence of
different reactive channels in the photochemistry of HCo(CO)₅ results from the crossing
of two potential energy surfaces, both dissociative.

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