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BOND ACTIVATION BY MLCT EXCITATION OF ORGANOMETALLIC COMPOUNDS: PROMPT CO-PHOTODISSOCIATION FROM [$Cr(CO)_4bpy$]

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Abstract

Dissociation of an axial CO ligand from $Cr(CO)_4bpy$ under irradiation into the MLCT absorption band is a prompt process that takes place from directly excited vibronic levels of the ^{1}MLCT state. Qualitative model of such processes based on a vibronic coupling between MLCT and LF states that activates promoting asymmetric vibration is proposed.

A. INTRODUCTION

Ligand dissociation induced by irradiation into metal to ligand charge transfer, MLCT, absorption band has been observed for various types of organometallic molecules. $Cr(CO)_4(\alpha,\alpha\text{-diimine})$ [1-4], $Cr(CNAryl)_6$ [5-6], $Fe(CO)_3(\alpha,\alpha\text{-diimine})$ [7], and $Fe(CO)_3(N_4Me_2)$ [8] are typical examples. This type of photoreactivity is usually characterized by a gradual increase of quantum yield, ϕ, with increasing excitation energy within the MLCT absorption band envelope. Its interpretation is, however, rather controversial. Ligand dissociation from directly excited MLCT states, from long-lived ^{3}MLCT states, or from LF states thermally populated via MLCT states have been proposed. Ligand dissociation directly from MLCT states is difficult to comprehend using simple bonding models, as the MLCT excitation creates "oxidized" metal atom and "reduced" ligand which behave as stronger acceptor and donor, respectively. Moreover, it is often the "spectator" ligand, CO, not directly involved in the MLCT transition, which photodissociates. To understand the intimate mechanism of the dissociative bond activation by MLCT excitation, we have performed detailed case study of the $Cr(CO)_4bpy$ complex, bpy = 2,2′-bipyridine, which is well known [1-4] to undergo dissociative substitution of the axial CO ligand both under excitation into the MLCT and LF absorption bands in the visible and near UV spectral regions, respectively.

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B. EXCITED STATE DYNAMICS

Picosecond time-resolved absorption spectra measured after 30ps, 532nm excitation into the MLCT absorption band (*i.e.* $d_\pi \rightarrow b_2(\pi^*$-diimine) transitions) revealed [4] the presence of two transients. One of them is formed completely within the excitation pulse and decays rapidly, $\tau \leq 50$ps. Its absorption is most prominent in the 500-575nm region. Based on its short lifetime and on the spectral similarity with the reduced $Cr(CO)_4(bpy^-)$ complex, this transient was assigned as a spin-singlet ^{1}MLCT excited state. The second transient is, for the most part, also formed within the excitation pulse. A small rise in its absorbance concomitant with the ^{1}MLCT decay was observed in several solvents. This transient is long-lived, $\tau \geq 100$ns, and its absorption extends above 580nm. It was assigned to the spin-triplet ^{3}MLCT state. Excitation at 355nm, directed to the LF absorption band, which partly overlaps with a higher MLCT(2) band (*i.e.* $d_\pi \rightarrow a_2(\pi^*$-diimine) transitions), yields only a low-intensity spectrum of the ^{3}MLCT state which is formed completely within the excitation pulse. No ^{1}MLCT absorption was detected, even at 20ps after the excitation. It may thus be concluded that both the LF state and the higher MLCT(2) state decay predominantly back to the ground state. The relaxation pathway to the lowest lying ^{3}MLCT state is inefficient and bypasses the ^{1}MLCT state. This observation also indicates a sub-picosecond lifetime of the LF state. The excited state dynamics is summarized by a Jablonski diagram presented in Figure 1.

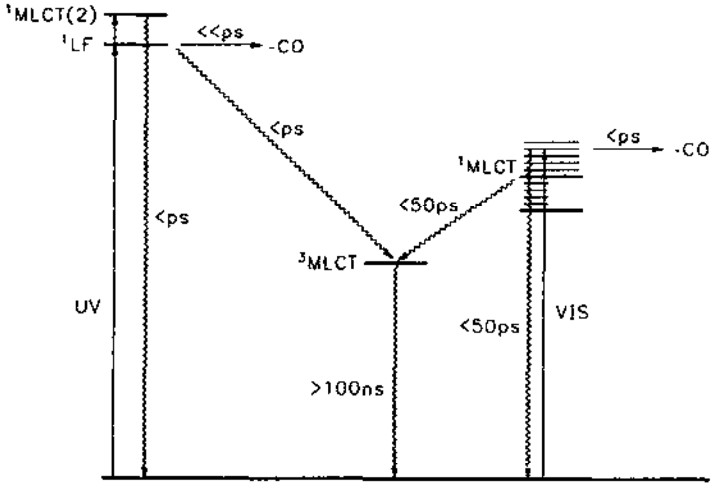

Figure 1. Excited state dynamics of $Cr(CO)_4$bpy.

C. PHOTOCHEMISTRY

Because of relatively low quantum yields, the formation of the $Cr(CO)_3bpy$ primary photoproduct could not be observed by time-resolved absorption spectra which are dominated by much stronger absorption of MLCT states. Hence, quantum yields of the reaction (1):

$$Cr(CO)_4bpy + PPh_3 \xrightarrow{h\nu} Cr(CO)_3(PPh_3)bpy + PPh_3 \qquad (1)$$

were measured as a function of excitation energy, solvent and temperature. Large excess of PPh_3 was used to ensure that the $Cr(CO)_3bpy$ primary photoproduct is completely converted to $Cr(CO)_3(PPh_3)bpy$, *i.e.* that the overall photochemical quantum yield is equal to the primary quantum yield of the CO dissociation.

Lack of any systematic solvent (toluene, CH_2Cl_2, C_6H_6, C_2Cl_4) influence on quantum yield values [4] indicates that the solvent does not affect the primary photoprocess significantly and that the solvent-cage effects are not important. Quantum yield values measured in toluene at 362, 497, and 557nm as a function of temperature [4] fit best the single-exponential Arrhenius-type equation, $\ln\phi=\phi_o\exp(-E_a/RT)$. This observation indicates that, at all excitation energies, the photoreactivity is dominated by a single electronic excited state, most probably by the A_1 MLCT state that results from the most intense $b_2(d_\pi)\rightarrow b_2(\pi^*\text{-bpy})$ transition. Dependencies of ϕ on the excitation energy [4] exhibit (Figs. 2, 3) two photoreactivity regions. The quantum yields are relatively large under near-UV excitation, sharply decreasing with the excitation wavelength. This region of large photoreactivity corresponds to the CO dissociation from the LF state. It occurs with very low activation energy and low preexponential factor. As the LF state decays on a subpicosecond timescale, the CO dissociation has to take place within few hundred femtoseconds, in order to be competitive. The second reactivity region occurs in the visible spectral region when the excitation is directed to the MLCT absorption band. Compared with the LF-reactivity, activation energies are larger and preexponential factors lower. Consequently, the ϕ-values are lower but still significant (about 10^{-2}) even under excitation into the low-energy end of the MLCT band. Importantly, quantum yields (both ϕ and ϕ_o) increase and activation energy decreases with increasing excitation energy within the MLCT absorption band envelope, Figs. 2, 3. These experiments show that the character of the reactive excited state is dependent on the excitation energy used. Hence, the CO dissociation cannot occur from the vibrationally relaxed ^{1}MLCT or from thermalized ^{3}MLCT states. Instead, it is suggested that the axial CO ligand dissociates from the directly excited (Franck Condon) vibronic levels of the ^{1}MLCT state. To be competitive with vibrational relaxation and with the decay (≤50ps) of the ^{1}MLCT state, the CO ligand must dissociate on a subpicosecond timescale.

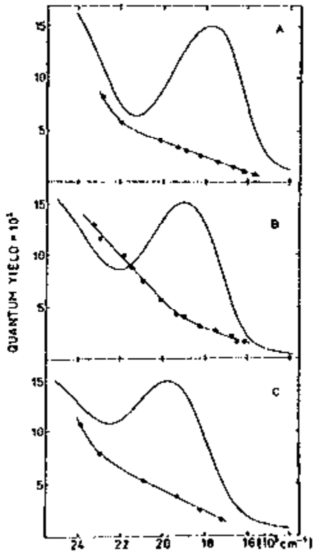

Fig. 2

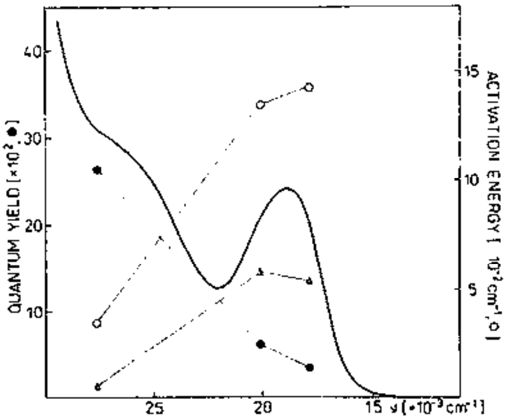

Fig. 3

Figure 2. Dependence of the quantum yields of reaction (1) on excitation energy and absorption spectra of $Cr(CO)_4bpy$ in different solvents at 21±0.1°C. (A) 6:1 (v/v) C_2Cl_4/C_6H_6 mixture, (B) C_6H_6, (C) CH_2Cl_2.

Figure 3. Dependence of the quantum yield (at 21±0.1°C), ϕ (●), activation energy, E_a (o), and preexponential factor, ϕ_o (Δ) on excitation energy. Measured in toluene.

D. Cr-CO BOND ACTIVATION BY MLCT EXCITATION

The excited state reactivity and dynamics of the $Cr(CO)_4bpy$ complex is summarized in Fig 1. However, it still remains to find out the factors responsible for such a rapid dissociation of the Cr-CO bond in the MLCT excited state. It has been shown [1] that the quantum yields of CO dissociation from $Cr(CO)_4$(diimine) complexes depend on the diimine ligand: phen (0.066) > bpy (0.054) > pyCaPh (0.0016) > DAB-p-tol (0.00024); phen = 1,10-phenanthroline, pyCaPh = pyridine-2-carbaldehyde-*N*-phenyl-imine, DAB-p-tol = *N,N'*-bis-*para*-tolyl-1,4-diaza-1,3-butadiene. Interestingly, mixing between d_π(Cr) and π^*(diimine) orbitals increases and, hence, the MLCT character of the electronic transition involved decreases in the same order, going from phen to DAB, [1,9]. Apparently, the CO dissociation becomes more efficient as the extent of the Cr→diimine charge transfer in the excited state increases. Another mechanistic insight is provided by the observation [2] that the quantum yield decreases 55-times going from $Cr(CO)_4$phen to $Cr(CO)_4(5\text{-}NO_2\text{-phen})$. The intensity of the MLCT absorption band of these two complexes is very similar indicating comparable extent of $d_\pi-\pi^*$ mixing. Hence, the decrease of electron density on the Cr atom caused by MLCT excitation is also expected to be comparable. However, in the latter species, the excited electron is localized mainly on the $-NO_2$ group, far from the reactive Cr-center. It thus appears that it is the localization of the excited electron in the π^*(diimine) orbital, rather than the positive "hole" on the Cr atom, that is responsible for the activation of the axial Cr-CO bond in the MLCT excited state.

Most importantly, the CO dissociation was shown to be a subpicosecond process that takes place from directly excited vibronic levels of the spin-singlet ^{1}MLCT excited state. This prompt character of the CO dissociation indicates substantial vibronic activation of the axial Cr-CO bond by the MLCT excitation. The B_2 asymmetric $(OC\text{-}Cr\text{-}CO)_{axial}$ stretching vibration, ν_{as}, appears to be the right vibration which, if activated, may lead to a dissociation of an axial CO ligand. Vibronic activation of ν_{as} is well conceivable as it couples the most intense $b_2(d_\pi)\rightarrow b_2(\pi^*)$ MLCT transition with the $b_2(d_\pi)\rightarrow a_1(d_\sigma*)$ LF transition which populates the dissociative LF state ($a_1(d_\sigma*)$ is the orbital oriented along the $(OC\text{-}Cr\text{-}CO)_{axial}$ axis, antibonding with respect to $Cr\text{-}CO_{ax}$ bonds). Consequently, the MLCT state acquires some dissociative LF character and its potential energy surface is significantly distorted, especially along the $Q_{as}=(1/\sqrt{2})(r_1-r_2)$ normal coordinate (r_1, r_2 are the lengths of the two Cr-CO bonds). This vibronic mixing between the MLCT and LF states may be simply visualized (Fig. 4) as a delocalization of the excited electron from the π^*(diimine) orbital to the $\sigma^*(M\text{-}C_{ax})$ orbital. Such a $\pi^*-\sigma^*$ interaction does not occur in the C_{2v} symmetry of the ground state but is made possible by the asymmetric distortion. This type of configurational interaction between MLCT and LF excited states gives rise to local minima on the MLCT surface at a geometry with unequal axial Cr-CO_{ax} bonds, $Q_{as} \neq 0$, as depicted in Fig. 5. At even larger asymmetric distortion, a region of avoided crossing with the dissociative LF state occurs, giving rise to an energy barrier to a complete dissociation of the Cr-CO_{ax} bond. Immediately after the

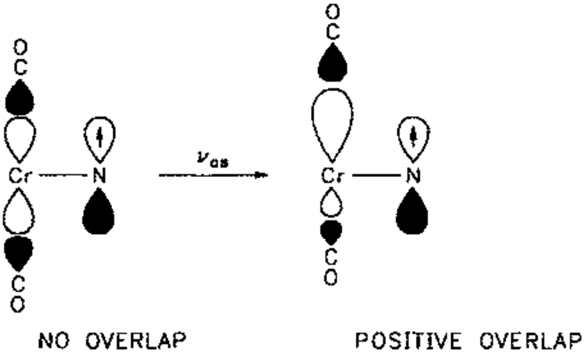

Figure 4. Effect of the asymmetric vibration, ν_{as}, on the π^*-σ^* interaction in MLCT-excited $Cr(CO)_4bpy$.

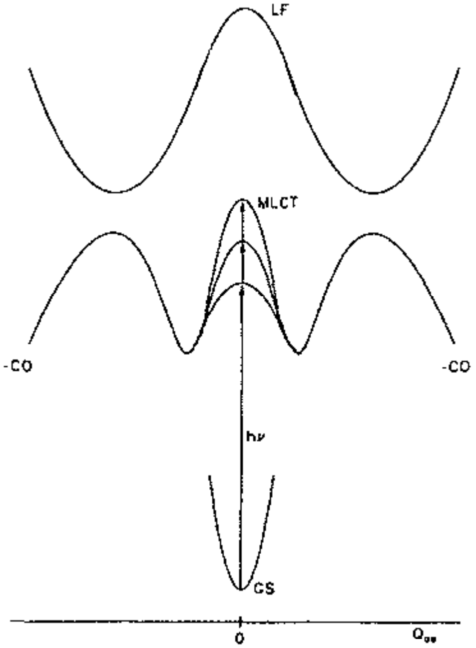

Figure 5. Potential energy surface of the reactive MLCT excited state along the Q_{as} coordinate (asymmetric axial OC-Cr-CO distortion)

vertical excitation, the initial wavepacket bifurcates and propagates downhill on both sides of the MLCT surface [10-12]. Fig. 5 shows that the higher the excitation energy, the steeper slope of the MLCT surface is experienced by the wavepacket very shortly after the excitation. Moreover, the MLCT-LF energy difference decreases with increasing excitation energy. For both these reasons, the amount of the dissociative LF character admixed into the directly excited MLCT state (see note [13]) and, hence, also the probability of the CO-dissociation are expected to increase monotonously with increasing excitation energy within the MLCT absorption band envelope. Indeed, this prediction agrees with experimentally observed dependence of the quantum yield on the excitation wavelength. Moreover, it is also quite evident from Fig. 5 that the energy barrier to be surmounted, and thus also the apparent activation energy, decreases with increasing excitation energy, again in accord with the experiment.

E. CONCLUDING REMARKS

The model proposed above to explain dissociative activation of the metal-ligand bonds upon the MLCT excitation assumes a coupling between optically excited MLCT state and higher dissociative LF state. This coupling is enabled by vibronically activated asymmetric stretching vibration that is also the promoting vibration for the bond dissociation. The photochemical reaction is a result of a very early excited state dynamics. This concept might be of more general importance in the photochemistry of transition metal compounds where strong coupling between excited states occurs because of high excited state density, many vibrational degrees of freedom, and large spin-orbit interaction. It thus appears that the use of simple (and convenient) configurational excited states labels (LF, MLCT, LMCT, *etc.*) as well as of the spin multiplicity might often be inadequate when interpreting very fast primary photoprocesses that are kinetically competitive with vibrational relaxation. Moreover, the conventional photophysical models based on temporally and energetically distinct relaxation processes (vibrational relaxation, internal conversion, ISC, *etc.*) also appears not to be generally applicable when ultrafast (fs-ps) photoprocesses are concerned. Obviously, prompt photoreactions present many open questions and their mechanistic investigation is a great challenge. Understanding of early excited state dynamics is a very important problem, as the overall course of photochemical reactions appears to be determined very shortly after the photon absorption.

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13. The mixing between MLCT and LF states in question may be approximated by following equation:

$$MLCT \approx MLCT_0 + \frac{\langle MLCT_0 | \frac{\partial V}{\partial Q} | LF \rangle}{E_{LF} - E_{MLCT_0}} \cdot Q \cdot LF$$

where $MLCT_0$ is the wavefunction of the "pure" MLCT state, $Q = Q_{as}$; V is the potential energy. The increase of the LF admixture into the MLCT wavefunction with increasing slope of the potential energy surface, increasing asymmetric distortion, and decreasing energy gap is obvious. Finally, it should be noted that the inverted shape [10-12] of the MLCT surface along Q_{as}, as depicted in Fig. 5, is not a necessary condition for the validity of the vibronic model of the CO dissociation. Identical conclusions may be inferred also under the assumption that the LF - MLCT coupling causes only a broadening (force constant decrease) and anharmonicity (result of LF-MLCT avoided crossing at larger distortion) of the MLCT surface.