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Direct Observation of Competitive Ultrafast CO Dissociation and Relaxation of an MLCT Excited State: Picosecond Time-Resolved Infrared Spectroscopic Study of $[Cr(CO)_4(2,2'\text{-bipyridine})]$

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Early excited-state dynamics of $[Cr(CO)_4(bpy)]$ were studied in a CH_2Cl_2 solution by picosecond time-resolved IR spectroscopy, which made it possible to characterize structurally the individual species involved and to follow separately the temporal evolution of the IR bands due to the bleached ground-state absorption, the *fac*-$[Cr(CO)_3(Sol)(bpy)]$ photoproduct, and two ^{3}MLCT states. It was found that the *fac*-$[Cr(CO)_3(Sol)(bpy)]$ photoproduct is formed alongside population of two ^{3}MLCT states during the first picosecond after excitation at 400 or 500 nm by a branched evolution of the optically populated excited state. Vibrationally relaxed ^{3}MLCT excited states are unreactive, decaying directly to the ground state on a picosecond time scale. The photoproduct is long-lived, persistent into the nanosecond time domain. Changing the excitation wavelength from 400 to 500 nm strongly increases the extent of the bleach recovery and decreases the yield of the photoproduct formation relative to the initial yield of the population of the unreactive ^{3}MLCT states. The photochemical quantum yield of CO dissociation also decreases with increasing excitation wavelength (Víchová, J.; Hartl, F.; Vlček, A., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 10903). These observations demonstrate the relationship between the early dynamics of optically populated excited states and the overall outcome of a photochemical reaction and identify the limiting role of the branching of the initial excited-state evolution between reactive and relaxation pathways as a more general principle of organometallic photochemistry.

Introduction

$[Cr(CO)_4(bpy)]$ is an excellent model complex for studying the structural and chemical effects of metal-to-ligand charge transfer (MLCT) electronic excitation, which leads to CO loss.[1−17] This is an intriguing case wherein optical charge transfer from the d^6 Cr(0) atom to the π-accepting bpy ligand induces dissociation of a spectator CO ligand that is accompanied by solvation (Scheme 1, top):

$$[Cr(CO)_4(bpy)] \xrightarrow{h\nu,\text{Sol}} fac\text{-}[Cr(CO)_3(Sol)(bpy)] + CO \qquad (1)$$

Similar dissociation of a CO ligand triggered by MLCT excitation is known for the $[M(CO)_4(\alpha\text{-diimine})]$ (M = Cr,

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Mo, W) congeners and other mixed-ligand carbonyl complexes such as [Mn(X)(CO)$_3$(α-diimine)], [Fe(CO)$_3$(α-diimine)], [Fe(CO)$_3$(1,4-Me$_2$N$_4$)], and [Ru(X)$_2$(CO)$_2$(α-diimine)].[9,14,15,17−27] Besides addressing fundamental questions about the mechanisms of photochemical bond activation, investigations of these reactions can reveal efficient ways to produce useful highly reactive, coordinatively unsaturated species. Previous studies of the photochemistry of [Cr(CO)$_4$(bpy)], and the closely related [Cr(CO)$_4$(phen)], have established the dissociative mechanism of the reaction 1 by observing that the quantum yield of photosubstitution is independent of the concentration of the incoming ligand, but is pressure-dependent, with a positive volume of activation.[15−17] The observation of the dependence of quantum yield on the excitation wavelength has indicated that CO dissociation is an ultrafast process, competitive with vibrational and electronic relaxation.[1,2] The primary photoproduct, *fac*-[Cr(CO)$_3$(Sol)(bpy)], has been detected by nanosecond time-resolved IR spectroscopy, which has also ruled out the presence of any long-lived (>10 ns) excited state.[3] Our previous study of the femtosecond time-resolved visible absorption spectra of [Cr(CO)$_4$(bpy)] has found[4] complicated ultrafast dynamics, involving the initial formation of several transient species in less than 400 fs, followed by a biexponential decay (8, 87 ps) that leaves a persistent spectrum attributed to a stable photoproduct *fac*-[Cr(CO)$_3$(Sol)(bpy)]. The early excited-state dynamics of [Cr(CO)$_4$(bpy)] and their relation to the overall photochemistry of this complex can only be fully understood through the use of a structure-sensitive time-resolved technique,[28] such as IR absorption. This can characterize the individual species involved and distinguish between their respective kinetic evolutions.

Experimental Section

The [Cr(CO)$_4$(bpy)] was prepared according to a modified[4] literature procedure, as described previously.[29] Spectroscopic quality CH$_2$Cl$_2$ and pyridine solvents were obtained from Aldrich.

The time-resolved spectroscopic techniques have been described in detail elsewhere.[28,30] In brief, a Ti:sapphire regenerative amplifier, operating at a 1 kHz repetition rate, produces 800 nm pulses of a ca. 200 fs duration (fwhm).[31] This laser output is split into two. One beam is frequency-doubled to produce 400 nm, 200 fs pulses. This beam is used either directly to pump the sample or to generate a 500 nm pump beam in an optical parametric amplifier. The second part of the 800 nm beam is directed to an optical parametric amplifier that uses difference frequency generation in an AgGaS$_2$ nonlinear material to provide ca. 200 fs IR probe pulses, tunable in the "fingerprint" range 1000−3000 cm^{-1}. The wavenumber bandwidth of the IR output is 150−200 cm^{-1}. The IR beam is further split into probe and reference beams. The pump and IR probe beams are focused to less than 200 μm diameter in the sample solution flowing through a 1 mm open jet, whereas the IR reference beam bypasses the sample. The relative timing of the arrival of the 400 or 500 nm pump pulses and broad-band IR probe pulses at the sample is set using an optical delay line that is placed in the pump beam optical path. The IR reference and probe beams travel by similar optical paths through two spectrometers where they are spectrally dispersed onto two Infrared Associates Inc. MCT-13-64el arrays of 64 elements each. All 128 signals from the arrays are preamplified (MCT-64000 Infrared Systems Development Corp.) and then captured by a custom-designed sample and hold analogue multiplexer system, the HX2, designed at the Rutherford Appleton Laboratory, before being read into a Datel 416J analogue-to-digital converter card inside a standard 500 MHz personal computer. The data are analyzed in pump on/pump off pairs at 1 kHz to create a rolling average of the difference IR absorbance values at each element. In this way, a ca. 150 cm^{-1} wide portion of a time-resolved IR difference absorption spectrum is obtained, sampled over 64 points. Broad-band spectra are constructed by overlapping the spectra measured over several ranges. Finally, each spectrum is shown as a difference between the spectrum measured at a given time delay after excitation by the pump pulse minus the spectrum obtained before excitation.

A time-resolved visible absorption spectrum was obtained using the same laser setup and a white-light continuum as the probe beam.[4,28,32] The measurement was performed on a flowing solution in a 2 mm cell.

Results and Discussion

Shown in Figure 1 are the picosecond time-resolved IR absorption spectra of [Cr(CO)$_4$(bpy)], measured from a CH$_2$Cl$_2$ solution at selected time delays after excitation with 400 nm (top) or 500 nm (bottom) laser pulses of ca. 200 fs duration. The positive absorptions correspond to photoproduced species, whereas the negative bands are due to the depletion of the [Cr(CO)$_4$(bpy)] ground state. All of these features are developed within the first picosecond after optical excitation.

The bleached [Cr(CO)$_4$(bpy)] absorption bands at 1829, 1881, 1901, and 2010 cm^{-1} mirror the ground-state spectrum. These bands correspond to the B$_2$, out-of-phase A$_1{}^1$, B$_1$, and in-phase A$_1{}^2$ CO stretching vibrations, respectively.[12] Their

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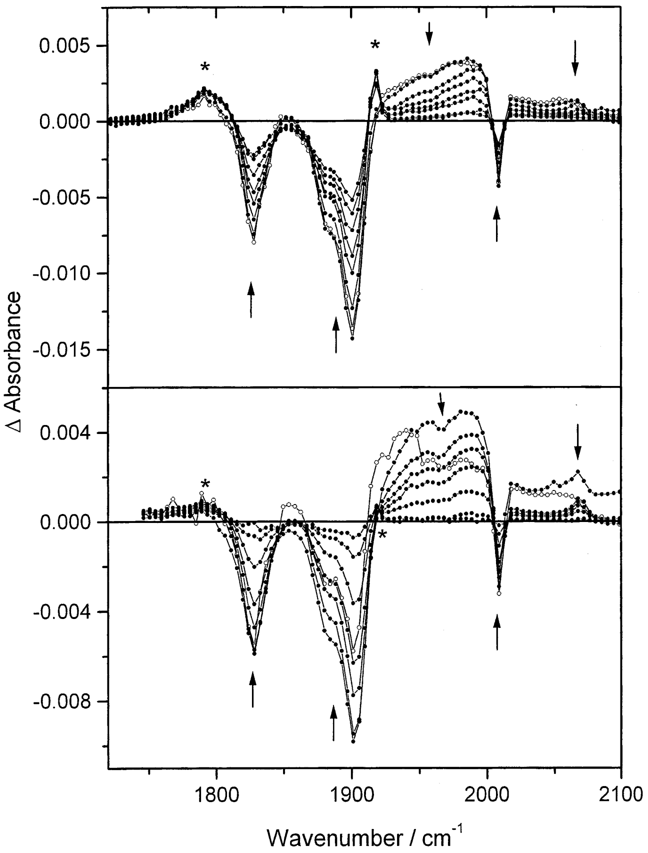

Figure 1. Time-resolved difference IR absorption spectra of [Cr(CO)$_4$(bpy)] in CH$_2$Cl$_2$ solution, measured at 1, 2, 10, 30, 50, 100, 200, and 1000 ps after excitation at 400 nm (top) or 500 nm (bottom). The arrows show the spectra evolution from 1 to 1000 ps. The 1 ps spectrum is shown with open circles (○). The asterisk (*) denotes the [Cr(CO)$_3$(CH$_2$Cl$_2$)(bpy)] photoproduct bands at 1916 and 1791 cm^{-1}. The negative and positive spectral features belong to bleached absorption of ground-state [Cr(CO)$_4$(bpy)] and the photoproduced species, respectively.

intensities decrease over the first 500 ps, due to partial recovery of the [Cr(CO)$_4$(bpy)] ground state, and then remain constant. The incomplete recovery demonstrates that some of the excited molecules undergo an irreversible photochemical reaction. The recovery kinetics are biexponential with lifetimes of 76 ± 7 and 8 ± 3 ps, as determined using 400 nm excitation. A lifetime of 80 ± 15 ps was obtained using 500 nm excitation with the short component being confirmed, but unresolved numerically.

The photoproduced species give rise to two, partially overlapping, IR spectral patterns. These are both present from the earliest times after excitation but have different temporal evolutions: one decaying, the other persistent. They are attributed to the simultaneously formed ^{3}MLCT excited state(s) and the *fac*-[Cr(CO)$_3$(Sol)(bpy)] photoproduct, respectively.

The decaying, transient, absorption pattern consists of a weak broad band at 2069 cm^{-1}, a broad feature between ca. 1920 and 2030 cm^{-1}, that has an apparent maximum at 1988 cm^{-1} and a shoulder at ca. 1950 cm^{-1}, and another feature at approximately 1850 cm^{-1}. (The latter feature becomes fully apparent only after the time-resolved spectrum is corrected for the bleached ground-state absorption. This was accomplished by a scaled numerical addition of the ground-state spectrum to the time-resolved difference spectrum. The intensity of the added spectrum was scaled commensurately to the intensity of the bleached 1901 cm^{-1} peak.) This spectral pattern can be attributed to a C_{2v} *cis*-tetracarbonyl species. The 2069 cm^{-1} is due to the in-phase A_1^2 vibration, the B_1 and A_1^1 modes give rise to the broad 1920−2030 cm^{-1} feature, and the ~1850 cm^{-1} band corresponds to the B_2 mode. These transient spectral features are shifted to higher wavenumbers by ca. 60−90 cm^{-1} relative to the corresponding ν(CO) bands of the ground state [Cr(CO)$_4$(bpy)]. This upward shift is characteristic[33−36] of a MLCT excited state and allows us to attribute the 2069, 1920−2030, and ~1850 cm^{-1} IR features to Cr → bpy ^{3}MLCT excited state(s) of [Cr(CO)$_4$(bpy)]. The increase of the ν(CO) wavenumbers on MLCT excitation is caused by a decrease of Cr → CO π back-donation, which diminishes the population of π^*(CO) orbitals. In agreement with this observation, the electron density on the four CO ligands was calculated to decrease by 0.24 e$^-$ upon Cr → bpy MLCT excitation.[8] Broadening of the transient IR features relative to the corresponding ground-state bands is also typical of MLCT excited states.[37]

The 2069, 1920−2030, and ~1850 cm^{-1} excited-state IR features are absent in the cross-correlation spectrum measured concomitantly with excitation, i.e., at $t = 0$. They are, however, fully developed in the 1 ps spectrum, in which they occur at somewhat lower wavenumbers than in the spectra measured at 2 ps and later. This fast spectral blue shift is larger for the 500 than 400 nm excitation, Figure 1. This emergence of the IR absorption features during the first picosecond and the subsequent small blue shift are most probably due to a combined effect of vibrational relaxation and solvation.[38] Decay kinetics were studied at 2069 cm^{-1} and at several wavenumbers in the 1930−1988 cm^{-1} range, where the IR absorption decays to the base line. The decay kinetics is biexponential with lifetimes that are, within the experiment accuracy, identical to those measured for the [Cr(CO)$_4$(bpy)] ground-state recovery. It follows that the ^{3}MLCT state(s) are unreactive, decaying directly and quantitatively to the ground state. The longer lifetime was determined as 67 ± 15 and 86 ± 7 ps using excitation wavelengths of 400 and 500 nm, respectively. These values agree very well with those measured by time-resolved visible absorption spectroscopy: 70 and 84 ps using 400 and 500 nm excitation, respectively.[4] The presence of the short-lived kinetic component was confirmed by comparing double- and single-exponential fits, although it was not always possible to measure its lifetime with a sufficient accuracy. This is apparently because of small changes in the IR band shapes

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at short time delays after excitation. Nevertheless, values of 5 ± 3 and 7 ± 3 ps were obtained using 400 and 500 nm excitation, respectively. This biexponential character of the decay kinetics points to the presence of two ^{3}MLCT states whose IR spectra overlap, contributing to the broadness of the transient IR features. Within the broad 1920−2030 cm^{-1} transient IR feature, it was found that the relative contribution of the short kinetic component increases 2−4 times when the probe wavenumber is changed from 1936 to 1990 cm^{-1}. It follows that, while the spectra of the two states overlap, the fast-decaying ^{3}MLCT state absorbs more strongly between 1936 and 1965 cm^{-1}, while the absorption of the longer-lived state predominates between 1970 and 1990 cm^{-1}. Previous CASSCF/CASPT2 calculations[11] have revealed the presence of two low-lying ^{3}MLCT triplet states a^3B_2 and a^3B_1 at 1.69 and 1.56 eV, respectively. They originate in Cr(d_{xy}) → π^*(bpy) and Cr(d_{z2-y2}) → π^*(bpy) MLCT principal excitations, respectively. (See Scheme 1 for orientation of axes.) Assuming that the higher state decays faster, we can assign the shorter-lived transient as a^3B_2 and the longer-lived one as a^3B_1.

The persistent, nondecaying, IR spectral pattern consists of a broad, weak band at 1791 cm^{-1} and a sharp, intense peak at 1916 cm^{-1}. Such a large peak separation and intensity pattern are characteristic of *facial* tricarbonyls, as opposed to their *meridional* isomers, for which an opposite band intensity ratio and peak separation of ca. 50 cm^{-1} are expected.[3] The 1791 and 1916 cm^{-1} bands are therefore attributed to the *fac*-[Cr(CO)$_3$(Sol)(bpy)] photoproduct; Sol = CH$_2$Cl$_2$. This assignment is further supported by the close correspondence between the 1791 and 1916 cm^{-1} bands observed herein with the IR spectrum of *fac*-[Cr(CO)$_3$(CH$_2$Cl$_2$)(bpy)] measured on the nanosecond time scale:[3] a sharp band at 1915 cm^{-1} and a broad band at 1786 cm^{-1} with a shoulder at ca. 1809 cm^{-1}. The strong band at 1916 cm^{-1} corresponds to the in-phase A′ vibration, while the A″ and out-of-phase A′ vibrations are nearly degenerate and merge together to form the broad IR band at 1791 cm^{-1}.

The temporal evolution of the 1916 and 1791 cm^{-1} bands shows that the formation of the *fac*-[Cr(CO)$_3$(Sol)(bpy)] photoproduct is ultrafast, occurring within the instrument time resolution of ca. 500 fs. Both IR bands are visible in the spectra measured at cross-correlation ($t = 0$) in which the ^{3}MLCT features are not yet fully developed, vide supra. The 1791 cm^{-1} band is directly seen in the 1 and 2 ps spectra (Figure 1), whereas the 1916 cm^{-1} band is obscured by an overlap with the intense negative band at 1901 cm^{-1} and the broad ^{3}MLCT feature. It becomes fully apparent only in spectra measured at 10 ps and later when the intensities of these overlapping features had diminished. Nevertheless, correction for the bleached ground-state absorption has confirmed the presence of the 1916 cm^{-1} photoproduct band also in the spectra recorded at 1 or 2 ps. The intensity of the 1791 cm^{-1} photoproduct band reaches 60−70% of its maximum value at 1 ps, corresponding to a ca. 400−500 fs rise time. Over the next 10 ps, it grows further and broadens slightly with an apparent rise time of 3.4 ± 1 ps. This behavior is due to the diminishing overlap with the decaying, negative, band at 1829 cm^{-1} and, possibly, to vibrational cooling and solvation. Later, between 70 and 500 ps, the 1791 cm^{-1} band intensity decreases slightly (≤10%) and then stays constant. The origin of this small decay remains unclear. It cannot be due to CO recombination since it was not observed for the 1916 cm^{-1} band. Neither of the intensity changes are accompanied by any shifts in the position of the 1791 cm^{-1} band maximum.

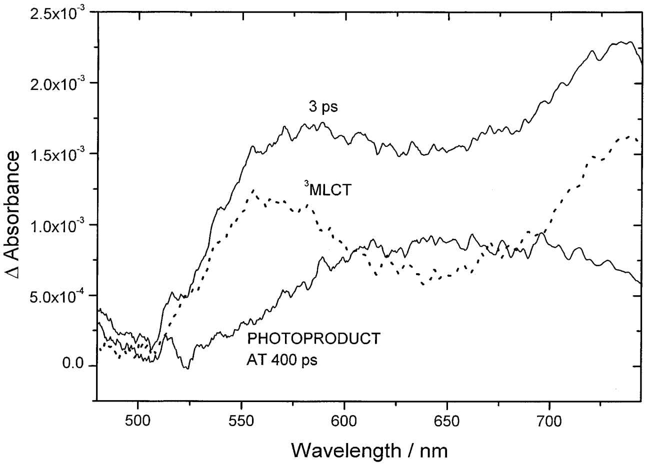

Figure 2. Time-resolved difference visible absorption spectra measured at 3 and 400 ps after excitation of [Cr(CO)$_4$(bpy)] in pyridine solution. The 400 ps spectrum belongs to the *fac*-[Cr(CO)$_3$(py)(bpy)] photoproduct. The dotted curve is the difference between the 3 and 400 ps spectra which corresponds to the ^{3}MLCT excited states. (The drop of absorbance below 550 nm is due to strong bleaching of the ground-state absorption.)

The simultaneous observation of IR bands due to the ^{3}MLCT excited states *and* the photoproduct in the 1 ps spectrum leads to the conclusion that the *fac*-[Cr(CO)$_3$(Sol)(bpy)] photoproduct is formed on a subpicosecond time scale, *concomitantly* with the population of the "trapping" ^{3}MLCT states, that are unreactive, decaying to the ground state.

These results justify our earlier assumption[4] that the visible absorption measured immediately after laser pulse excitation of [Cr(CO)$_4$(bpy)] is a sum of the spectra of the "trapping" ^{3}MLCT excited states and the photoproduct. This is shown in Figure 2 where the 400 ps spectrum is assigned to the *fac*-[Cr(CO)$_3$(Sol)(bpy)] photoproduct and the difference between the 3 and 400 ps spectra (dotted line) corresponds to the ^{3}MLCT states. The characteristic red absorption of the bpy$^{\bullet-}$ chromophore[39,40] is clearly visible above 650 nm, further confirming the assignment of the decaying transient as ^{3}MLCT.

Further insight into the mechanism of photochemical CO dissociation (eq 1) can be gained from the comparison of the TRIR spectra obtained using 400 and 500 nm excitation. Qualitatively, the observed spectral features and their temporal evolutions are the same, except for a small difference in the value of the longer lifetime, 67 and 86 ps, respectively. However, a more detailed comparison of the two sets of spectra (Figure 1) shows three important differences: (i) The extent of the [Cr(CO)$_4$(bpy)] ground-state recovery is much higher after 500 nm than 400 nm excitation, reflecting the

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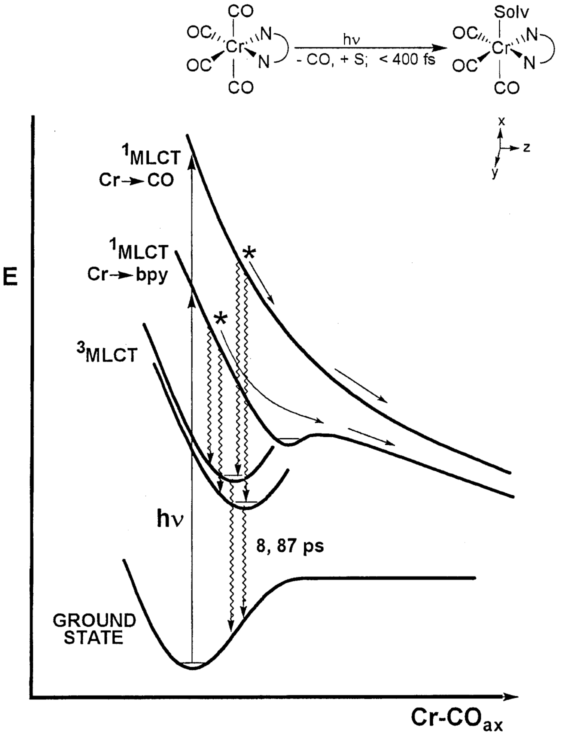
decrease of the quantum yield of the photochemical CO dissociation with increasing irradiation wavelength.[1] (ii) The ratio of the intensities of the 1916 cm^{-1} *fac*-[Cr(CO)$_3$(Sol)(bpy)] photoproduct band measured at 1000 ps and of the 1988 cm^{-1} band of the ^{3}MLCT excited states at 1 ps decreases approximately 3 times (a crude estimate) on changing the excitation wavelength from 400 to 500 nm, reflecting the decrease of the branching ratio between the CO dissociation from the optically populated excited state and its relaxation to the unreactive ^{3}MLCT states. This decrease of the branching ratio with increasing irradiation wavelength parallels the decrease of the CO photodissociation quantum yield.[1] (iii) The change of the shape and position of the IR absorption of the ^{3}MLCT excited state between 1 and 2 ps is much larger after excitation at 500 than 400 nm. This effect may be explained by different rates of vibrational relaxation that could be faster after 400 nm than 500 nm excitation. Accompanying IR band shifts and narrowing would then be largely completed in the first picosecond in the former case but still well observable in the 1−2 ps interval after 500 nm excitation.

Scheme 1. Dynamics of MLCT Excited States of [Cr(CO)$_4$(bpy)]: Branching of the Evolution of the Optically Populated ^{1}MLCT Excited States between Dissociation and Relaxation Pathways[a]



[a] The photochemical reaction is shown above the diagram, together with the coordinate system used to define the Cr d orbitals. The asterisks (*) designate branching between the reaction and relaxation, which was directly demonstrated herein by picosecond TRIR spectroscopy using excitation at 400 nm (top) and 500 nm (bottom). Excitation at 400 nm populates both the Cr → bpy and Cr → CO ^{1}MLCT states while the Cr → bpy ^{1}MLCT state only is populated at 500 nm. Both ^{1}MLCT potential energy surfaces are (nearly) dissociative due to a strongly avoided crossing with a higher-lying ^{1}LF state, which occurs along the reaction coordinate.[2,10,11] The small barrier on the Cr → bpy ^{1}MLCT surface is evidenced by the temperature dependence of the photochemical quantum yield.[1] The 8 and 87 ps trapping ^{3}MLCT states are assigned as a^{3}B$_2$ and a^{3}B$_1$ respectively.[11] They originate in Cr(d$_{xy}$) → π*(bpy) and Cr(d$_{z2-y2}$) → π*(bpy) principal excitations, respectively.[11]

The picosecond time-resolved IR spectroscopic experiments described above have allowed us to unambiguously establish the mechanism of the photochemical Cr−CO bond dissociation in [Cr(CO)$_4$(bpy)] and reveal the direct relation between the early excited-state dynamics and the overall photochemistry of this complex. This is shown in Scheme 1, which also incorporates results of our previous spectroscopic, theoretical, and photochemical studies.[1,3,4,10,11] The UV−vis absorption spectrum of [Cr(CO)$_4$(bpy)] in CH$_2$Cl$_2$ shows an intense band at 490 nm due to the Cr(d$_{xz}$) → bpy MLCT transition[1,4,10,11] and a shoulder at 400 nm that was attributed to the Cr → CO MLCT transition(s).[7,10,11,41] Hence, 500 nm excitation leads only to the Cr → bpy ^{1}MLCT b^{1}A$_1$ excited state, while both Cr → CO and Cr → bpy ^{1}MLCT states are populated at 400 nm.[10,11] Optical excitation into the Cr → bpy ^{1}MLCT is immediately followed by ultrafast evolution either along the dissociative pathway, toward the *fac*-[Cr(CO)$_3$(Sol)(bpy)] photoproduct, or along the relaxation pathway to the two lower-lying Cr → bpy ^{3}MLCT excited states, as was manifested herein by the simultaneous appearance of the corresponding IR features during the first picosecond. The ^{3}MLCT states decay directly and completely to the ground state with lifetimes of 8 and 87 ps. (These values are valid for visible-light excitation.[4]) They do not undergo any CO dissociation, behaving as "trapping states". The observation of IR bands belonging to the *fac*-[Cr(CO)$_3$(Sol)(bpy)] photoproduct already at 1 ps rules out any major structural reorganization following the CO dissociation. This observation demonstrates the prompt and stereospecific character of the dissociation of an axial CO ligand and its occurrence directly from the optically populated ^{1}MLCT excited state(s). Solvation by CH$_2$Cl$_2$ is probably very fast, involving a solvent molecule that is present in the first solvation sphere already at the instant of the optical excitation. The optically populated Cr → CO ^{1}MLCT state appears to behave similarly to the Cr → bpy b^{1}A$_1$ state discussed above, see Scheme 1, upper potential energy surface. Molecules in the Cr → CO ^{1}MLCT excited state undergo either relaxation to the two trapping Cr → bpy ^{3}MLCT states or CO loss to form the *fac*-[Cr(CO)$_3$(Sol)(bpy)] photoproduct, both of these processes being completed in less than 1 ps. Temperature and pressure dependences of the quantum yield suggest that there is hardly any communication between the reactive Cr → CO and Cr → bpy ^{1}MLCT states since two distinct reactivity pathways were observed using near-UV and visible irradiation.[1,15−17]

The TRIR experiments also show that branching of the evolution of the optically prepared ^{1}MLCT states between CO dissociation and relaxation is completed in less than 1 ps. Our previous femtosecond time-resolved visible absorption[4] and theoretical[10] studies allow us to narrow this interval further, to less than 400 fs. The CO dissociation and relaxation processes are competitive, parallel processes. In the absence of any photoproduct recombination, it is this ultrafast branching of the excited-state evolution that determines the overall photochemical quantum yield, ϕ. This can

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be expressed as $\phi = a/(a + \sum b_i)$, where a is the number of dissociated molecules and b_i is the number of molecules which relax to the ^{3}MLCT state i. For $\phi \ll 1$, the quantum yield becomes equal to the branching ratio, $\phi \cong a/\sum b_i$. The approximately 3-fold decrease of the branching ratio on increasing the excitation wavelength from 400 to 500 nm, estimated from TRIR, agrees with the 2.94-fold drop of the quantum yield that was measured using steady-state irradiation.[1] Moreover, this direct observation of the branching ratio decrease with increasing irradiation wavelength confirms the conclusion of our previous study[4] of the femtosecond time-resolved visible absorption spectra of [Cr(CO)$_4$(bpy)], where the branching ratio was determined indirectly from kinetic parameters. A 2.3-fold decrease of the branching ratio between 400 and 500 nm excitation was found,[4] again in good agreement with the present study.

It should be noted that, unlike femtosecond time-resolved visible absorption spectroscopy or steady-state quantum-yield measurements, picosecond TRIR spectroscopy allows us to examine the branching process directly, without any preliminary assumptions about the reaction mechanism. This is made possible by the ability of TRIR spectroscopy to observe and characterize separately the photoproducts and excited states involved in photochemical mechanisms.

In conclusion, the TRIR study of the excited-state dynamics of [Cr(CO)$_4$(bpy)] has demonstrated that the optically populated ^{1}MLCT excited state(s) undergo two parallel prompt processes: highly stereospecific dissociation of an axial CO ligand and relaxation to two unreactive ^{3}MLCT states. These ^{3}MLCT trapping states then decay to the ground state on the picosecond time scale. The photochemical quantum yield is limited by the branching ratio between the reactive and relaxation pathways, demonstrating the relation between the initial excited-state dynamics and overall photochemistry. The limiting role of the branching of the initial excited-state evolution in determining organometallic photochemical reactivity appears to be an emerging general principle, applicable to other classes of compounds, for example to CO dissociation from cyclopentadienyl−carbonyl complexes involved in photochemical C−H activation[42−47] or Re−R homolysis in diimine−alkyl complexes.[48]

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