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Photophysical Features of the $M_2(CO)_{10}$, M = Mn and Re, Solution Photochemistry

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Introduction

The solution phase photochemistry of metal−metal-bonded carbonyl complexes, $M_2(CO)_{10}$, M = Re or Mn, have been the subject of numerous studies.[1−4] Two primary photoprocesses, the homolytic dissociation in pentacarbonyl radicals, eq 1, and the photoelimination of CO, eq 2, have been reported for these complexes. When appropriate scavengers of these coordinatively unsaturated products are not available, they regenerate the decacarbonyl complex via termination reactions, eqs 3 and 4.

$$M_2(CO)_{10} + h\nu \xrightarrow{\phi_P} 2M(CO)_5 \qquad (1)$$

$$M_2(CO)_{10} + h\nu \xrightarrow{\phi_N} M_2(CO)_9 + CO \qquad (2)$$

$$2Re(CO)_5 \xrightarrow{k_R} Re_2(CO)_{10} \qquad (3)$$

$$M_2(CO)_9 + CO \rightarrow M_2(CO)_{10} \qquad (4)$$

The 366 nm photolyses of $Re_2(CO)_{10}$ in solutions of olefins (styrene, *trans*-stilbene, 4-methyl-1-cyclohexane, and ethylene) yield hydride alkenyl dirhenium octacarbonyl complexes, (μ-H)(μ-alkenyl)$Re_2(CO)_8$, as major photoproducts.[5−7] Such photoproducts result from reactions of the olefin with $Re_2(CO)_9$. No reactions of $Re(CO)_5$ leading to hydride alkenyl products were observed. Moreover, flash photolysis has shown the presence of several intermediates in the mechanism of (μ-H)(μ-alkenyl)$Re_2(CO)_8$ formation.[7]

Literature values of the ratio of the quantum yields, $\phi_P/(2\phi_N)$, for the Mn carbonyl show that the photoelimination of CO, eq 2, is favored with decreasing wavelengths.[8] The photobehavior of $M_2(CO)_{10}$, M = Re or Mn, as a function of the irradiation wavelength was investigated in this work by the flash-photochemical determination of the quantum yields for each metalloproduct in eqs 1 and 2.

Experimental Section

Time-Resolved Optical Measurements. Time-resolved reaction kinetics and optical spectra recorded at times longer than 10 ns were investigated with a modification of the flash photolysis apparatus described in the literature.[7] Laser pulses of 308 and 248 nm were generated with an excimer laser (Lambda Physik), those with 355 and 266 nm with a Nd:Yag laser (Quanta Ray), and the 337 nm pulses with a N_2 laser (Laser Photonics, PRA/model UV-24).[9] The flash photolysis apparatus used for experimental observations between 20 ps and several nonaseconds has been described elsewhere.[10] Solutions for flash photolysis were prepared by adding solid $M_2(CO)_{10}$, M = Re or Mn, to Ar-deaerated solutions of the reactants in CH_3CN. The liquids in a gastight cell were handled under Ar. A 15 cm^3 volume of solution was stirred after each flash irradiation and used for only 10 consecutive experiments. Light intensities in laser-flash irradiations were measured with $Co(NH_3)_5Br^{2+}$ by a literature procedure.[11] Quantum yields in flash photolysis were calculated with such intensities and the corresponding concentrations of the primary photoproducts appraised from the oscillographic traces. Other conditions for these measurements are descrobed elsewhere in Results.

Materials. [Cu(Me_4-[14]-1,3,8,10-tetraeneN$_4$)]$(ClO_4)_2$ and [Co$(NH_3)_5$Br]Br_2 were available from previous work and used without further purification.[10,11] $M_2(CO)_{10}$, M = Re and Mn, were obtained 99.99% pure from Jansen Chemicals. Vacuum sublimations were applied to the purification of $Re_2(CO)_{10}$ according to a literature procedure. Results from flash photochemical experiments with this purified material and reagent grade $Re_2(CO)_{10}$ were not different. The Aldrich, spectroquality solvents, CH_3CN and cyclohexane, and O_2-free Ar were used without further purification for the preparation of solutions.

Results

Characteristic absorption bands of the nonacarbonyl, $Re_2(CO)_9$ with $\lambda_{max} < 360$ nm, and pentacarbonyl, $Re(CO)_5$ with $\lambda_{max} = 550$ nm, complexes were observed after laser flash irradiations of deaerated $Re_2(CO)_{10}$ in cyclohexane. Scavenging of the nonacarbonyl by acetonitrile in deaerated solutions produced $Re_2(CO)_9CH_3CN$, a stable product whose absorption spectrum shows a maximum at 320 nm. The previously investigated reaction of the pentacarbonyl with Cu(Me_4-[14]-1,3,8,10-tetraeneN$_4$)Cl^+, eq 5, was used for the determination of the pentacarbonyl quantum yield.[12] On the basis of this reaction's 1:1 stoichiometry, the concentrations of Cu(Me_4-[14]-1,3,8,10-tetraeneN$_4$)$^+$, [Cu(Me_4-[14]-1,3,8,10-tetraeneN$_4$)$^+$]$_{lim}$, and flash-generated pentacarbonyl in eq 5 were considered equal when $Re(CO)_5$ was scavenged with a 100% efficiency by Cu(Me_4-[14]-1,3,8,10-tetraeneN$_4$)Cl^+, i.e., for concentrations of the Cu(II) complex equal to or larger than 10^{-3} M. The Cu(Me_4-[14]-1,3,8,10-tetraeneN$_4$)$^+$ concentration was established from its absorption at 740 nm ($\epsilon = 8000\ M^{-1}\ cm^{-1}$), a wavelength where the parallel formation of $Re_2(CO)_9CH_3CN$ introduced no analytical complications. Quantum yields of the pentacarbonyl

$$Re(CO)_5 + Cu(Me_4\text{-}[14]tetraeneN_4)Cl^+ \rightarrow Re(CO)_5Cl + Cu(Me\text{-}[14]tetraeneN_4)^+ \qquad (5)$$

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Table 1. Nonacarbonyl and Pentacarbonyl Quantum Yields in Photolyses of $M_2(CO)_{10}$, M = Mn and Re, Compounds

irradn wavelength, nm	$\phi_P{}^a$	$\phi_N{}^a$	$\phi_P/(2\phi_N)^a$
	$Mn_2(CO)_{10}$		
355	0.24	0.12	1.0 1.1^b
347			0.43^c
337	0.33	0.34	0.49 0.43^b
308	0.12	0.57	0.11
266	0.26	0.64	0.20 0.21 ± 0.07^b
	$Re_2(CO)_{10}$		
355	0.35	0.18	0.97
337	0.49	0.43	0.57
308	0.20	0.10	1.0
266	0.48	0.20	1.2
248	0.39	0.27	0.72

[a] Quantum yields in deaerated cyclohexane unless stated. Values correspond to an average of three determinations with errors equal to or less than 10%. [b] Determined in cyclohexane. Values taken from ref 8. [c] Determined in ethanol. Value taken from ref 14.

product were calculated with eq 6, for irradiations at various wavelengths. The number of photons absorbed by $Re_2(CO)_{10}$,

$$\phi_P = \frac{[\mathrm{Cu(Me_4\text{-}[14]tetraeneN_4)^+}]_{\mathrm{lim}}}{I_{ab} \times \Delta t} \tag{6}$$

$I_{ab} \times \Delta t$, was measured in separate experiments by measuring the concentration of $Br_2^{\bullet -}$ radicals, $[Br_2^{\bullet -}]$ in eq 7, generated when the actinometer, $Co(NH_3)_5Br^{2+}$, was flash-irradiated in deaerated acidic solutions that were also decimolar in Br^- ions.

$$I_{ab}'\Delta t = \frac{[Br_2^{\bullet -}]}{\phi_{CT}} \tag{7}$$

Concentrations of $Co(NH_3)_5Br^{2+}$ were adjusted for each particular irradiation wavelength in order to make $I_{ab} = I_{ab}'$ in eqs 6 and 7. Literature quantum yields, ϕ_{CT}, for the formation of Br_2^- in the wavelength-dependent photoredox decomposition of the Co(III) complex were used with eq 7. According to this procedure, a 0.35 quantum yield of pentacarbonyl formation, ϕ_P, was calculated for the 355 nm irradiations of $Re_2(CO)_{10}$, Table 1. A similar value resulted when $Re_2(CO)_{10}$ was flash-photolyzed in a cyclohexane solution. The initial concentration of $Re(CO)_9$ was determined from the optical density change at 535 nm immediately after the 15 ns laser flash. A literature value of the extinction coefficient in ethanol, $\epsilon_{535\ \mathrm{nm}} = 1000$ M^{-1} cm^{-1}, was used for these calculations.[1] The 355 nm quantum yield of $Re(CO)_5$, Table 1, and a published ratio of pentacarbonyl to nonacarbonyl quantum yields, $\phi_P/(2\phi_N) = 0.15$,[8,13] results in a nonacarbonyl yield of $\phi_N = 1.17$. The overall quantum yield for the photoreactions, $^1/_2\phi_P + \phi_N \approx 1.34$, is therefore larger than unity. Similar results were obtained for photolysis of $Re_2(CO)_{10}$ in cyclohexane. The reason for these observations and discrepancies between published quantum yields and those in this work stems from an erroneous extinction coefficient for $Re_2(CO)_9$ in the literature.[8] Such an error in the extinction coefficient appears to be related to recently observed reactions of a nonacarbonyl precursor and a faulty trapping of $Re_2(CO)_9$ by CO.[7] The extinction coefficient of the nonacarbonyl at 400 nm was measured in this work from the spectroscopic determination of the stable $Re_2(CO)_9$(4-benzoylpyridine) product formed in the quantitative trapping of $Re_2(CO)_9$, eq 8. Flash

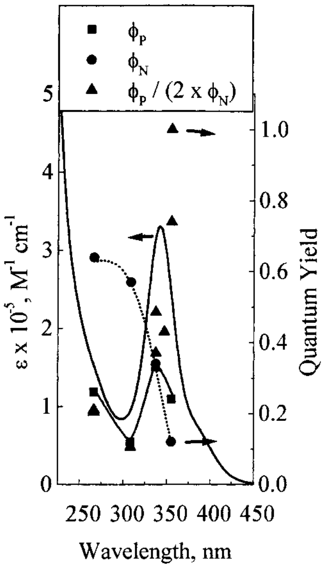

Figure 1. $Mn_2(CO)_{10}$ optical absorption spectrum and action spectra based on the quantum yield of penta- (ϕ_P) and nonacarbonyl (ϕ_N) photoproducts.The ratio between quantum yields ($\phi_N/2\phi_P$) is also plotted vs the excitation wavelength.

$$Re_2(CO)_9 + \text{4-benzoylpyridine} \rightarrow Re_2(CO)_9(\text{4-benzoylpyridine}) \tag{8}$$

irradiations of 3×10^{-4} M $Re_2(CO)_{10}$ in cyclohexane in the presence of 1.0×10^{-2} M 4-benzoylpyridine led to a growth of the 400 nm optical density. The same spectral change, associated with the $Re_2(CO)_9$(4-benzoylpyridine) formation in eq 8, was observed when $Re(CO)_5$ was quantitatively scavenged with 5.0×10^{-2} M hexachloroethane in parallel with the trapping of $Re_2(CO)_9$ with 4-benzoylpyridine. Therefore, $Re(CO)_5$ does not react with 4-benzoylpyridine and makes no contribution to the nonacarbonyl concentration under these experimental conditions.[7] On the basis of the stoichiometry of eq 8 and a reported value of the $Re_2(CO)_9$(4-benzoylpyridine) extinction coefficient at 403 nm, $\epsilon_{403\mathrm{nm}} = 4 \times 10^3$ M^{-1} cm^{-1} in hexane,[14] a coefficient of $\epsilon_{400\mathrm{nm}} = (2.8 \pm 0.5) \times 10^3$ M^{-1} cm^{-1} was calculated for the rhenium nonacarbonyl. Quantum yields of $Re_2(CO)_9$ were also calculated with eq 9 on the basis

$$\phi_N = \frac{[Re_2(CO)_9(\text{4-benzoylpyridine}]}{I_{ab}t} \tag{9}$$

of the stoichiometry in eq 8 and the actinometric measurements of $I_{ab}\Delta t$ that were described above. The directly measured quantum yield of the nonacarbonyl, Table 1, resulted in $^1/_2\phi_P + \phi_N$ values smaller than 1 in accordance with mechanistic expectations.

Procedures similar to those indicated above were used in flash photolyses of $Mn_2(CO)_{10}$ in deaerated cyclohexane for the determination of the nonacarbonyl, $\epsilon_{500\ \mathrm{nm}} = 1 \times 10^3$ M^{-1} cm^{-1} in hexane,[15] and pentacarbonyl, $\epsilon_{830\ \mathrm{nm}} = 9.5 \times 10^2$ M^{-1} cm^{-1} in hexane,[16] quantum yields, Table 1. The ratio of the measured quantum yields, Figure 1, gave values of $\phi_P/(2\phi_N)$ showing

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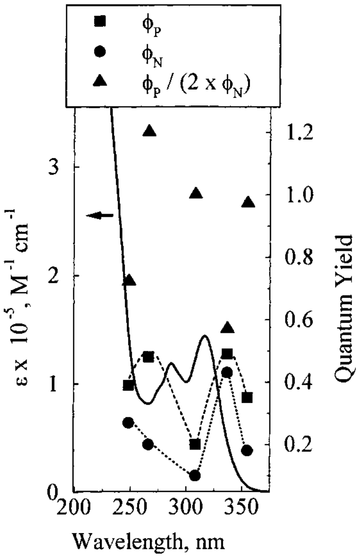

Figure 2. $Re_2(CO)_{10}$ optical absorption spectrum and action spectra based on the quantum yield of penta- (ϕ_P) and nonacarbonyl (ϕ_N) photoproducts. The ratio between quantum yields ($\phi_N/2\phi_P$) is also plotted vs the excitation wavelength.

moderate agreement, in spite of solvent differences, with those in a literature report.

The photogeneration of pentacarbonyl products in 266 nm irradiations of the Mn and Re decacarbonyl complexes was also investigated in a picosecond to nanosecond time domain. Time-resolved spectra demonstrate that $M(CO)_5$, M = Mn or Re, are formed faster than the 20 ps response of our flash photolysis instrument.

Discussion

The action spectra based on the nona-, ϕ_N, and pentacarbonyl, ϕ_P, quantum yields and their ratio, $\phi_P/(2\phi_N)$, are shown in relationship to the corresponding absorption spectra in Figures 1 and 2.[17,18] While the quantum yield of $Mn(CO)_5$ reaches a maximum value within wavelengths of the 340 nm band in the absorption spectrum, the $Mn_2(CO)_9$ quantum yield increases with decreasing irradiation wavelength. These experimental observations and the functional dependence of $\phi_P/(2\phi_N)$ on the wavelength of irradiation suggest that the two primary photoprocesses, eqs 1 and 2, may be started in the low-lying excited states but that upper states preferentially form the nonacarbonyl product. In the gas phase photochemistry of $Mn_2(CO)_{10}$, only the photogeneration of nonacarbonyl is observed by excitation to the upper electronic states.[19] In a theoretical calculation,[20] the difference between gas and solution phase photochemistry has been rationalized by assuming a solvent-induced relaxation of the upper states to a lower $^3\sigma\sigma^*$ excited state, i.e., one responsible for the formation of $Mn(CO)_5$. While the theoretical calculations account for the observations in the gas phase, they have not included the role of the solvent in shaping potential surfaces and its participation in elementary photophysical and photochemical processes.The validity of those calculations in solution phase photochemistry is therefore questionable. Present experimental evidence in condensed phase does not unequivocally establish that, in irradiations below 300 nm, all the $Mn(CO)_5$ product is formed in the $^3\sigma\sigma^*$ state, i.e., after the nonradiative relaxation of the upper electronic states to the $^3\sigma\sigma^*$ state. In the photochemistry of $Re_2(CO)_{10}$, the action spectra for the photoproducts, Figure 2, cannot be rationalized on the basis of the mechanism proposed for the photochemistry of $Mn_2(CO)_{10}$. These spectra do not conform to the proposition that, in irradiations below 300 nm, all the $Re(CO)_5$ produced resulted from the relaxation of upper electronic states to the lower lying $^3\sigma\sigma^*$ state. Moreover, the minimum in the action spectrum near 300 nm suggests that excited states populated at such wavelengths do not efficiently convert to and must be less photoreactive than a lower lying $^3\sigma\sigma^*$ state. This may explain also the displacement of the action spectra with regard to the first absorption band. The formation of $Re(CO)_5$ in upper electronic states, i.e., populated by irradiation at wavelengths shorter than 300 nm, is suggested by the action spectra.

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