in Figure 6B. The presence of both couples in the film is evidenced by the waves that appear at +0.88 and +0.70 V corresponding to the $Ru^{III/II}$ and $Fe^{III/II}$ couples, respectively. By integration, the ratio of Fe^{2+} to Ru^{2+} in the copolymeric film was 16:84.

Copolymerization of $[Ru(bpy)_2(4,4'-(CH_2Br)_2bpy)]^{2+}$ and $[Os(vbpy)_3]^{2+}$. A solution 1.08 M in $[Ru(bpy)_2(4,4'-(CH_2Br)_2bpy)^{2+}$ and 0.73 M in $[Os(vbpy)_3]^{2+}$ (60:40 Ru^{II}:Os^{II}) was electropolymerized by scanning the potential to −1.4 V. At this potential only the Ru^{2+} complex was reduced. This experiment was conducted to see if copolymerization could be induced by selective reduction at the Ru^{2+} complex. In the cyclic voltammogram of the resulting film reversible waves appeared at +0.41 and +1.00 V for the $Os^{III/II}$ and $Ru^{III/II}$ couples, respectively. By integration, the ratio of Ru^{II} to Os^{II} was 73:27. In a control experiment in which there was only $[Os(vbpy)_3]^{2+}$ in the polymerization solution, no significant electropolymerization was observed.

Layered Structures. In order to facilitate this part of the presentation, layered structures will be represented in the format: electrode/component 1/component 2. In this representation component 1 is the initially electropolymerized monomer. After electropolymerization, it is at the electrode/film interface. Component 2 is the monomer that was electropolymerized as a second film, atop the first, in a second step. After the second electropolymerization it is at the film/solution interface.

Pt/$[Fe(4,4'-(CH_2Br)_2bpy)_3]^{2+}$/$[Ru(bpy)_2(4,4'-(CH_2Br)_2bpy)]^{2+}$. The preparation of an inner layer of electropolymerized $[Fe(4,4'-(CH_2Br)_2bpy)_3]^{2+}$ ($\Gamma = 5.4 \times 10^{-9}$ mol/cm^2) was carried out initially. This step was followed by the electropolymerization of $[Ru(bpy)_2(4,4'-(CH_2Br)_2bpy)]^{2+}$ in a second step. A cyclic voltammogram for the resulting "bilayer" is shown in Figure 7A. In the voltammogram, waves for both the $Ru^{III/II}$ and $Fe^{III/II}$ couples were observed. The reductive component for the $Ru^{III/II}$ wave appeared as a sharp prepeak at the onset of the reductive component for the $Fe^{III/II}$ wave. This is due to an enhancement in the rate of reduction of the Ru^{3+} in the outer layer. At the onset of reduction of Fe^{3+} in the inner layer, the Fe^{2+} produced can, in turn, reduce Ru^{3+}, which is spatially isolated in the outer layer. Thus, reduction of Ru^{3+} is mediated by Fe^{2+}. This behavior is in contrast to the copolymeric film in Figure 6A where neither of the component waves is distorted. Both components are in the inner layer and have direct channels for undergoing electron transfer with the electrode surface.

Pt/$[Fe(4,4'-(CH_2Br)_2bpy)_3]^{2+}$/$[Ru(vbpy)_3]^{2+}$. An inner layer of electropolymerized $[Fe(4,4'-(CH_2Br)_2bpy)_3]^{2+}$ ($\Gamma = 7.8 \times 10^{-9}$ mol/cm^2) was prepared on a Pt electrode. In a second electropolymerization step an outer layer of polymerized $[Ru(vbpy)_3]^{2+}$ was added. A cyclic voltammogram of the resulting film is shown in Figure 7B. The overlap between the $Ru^{III/II}$ and $Fe^{III/II}$ waves is greater than in the previous case. A sharp prepeak is still observed at the onset of the $Fe^{III/II}$ reduction due to the mediated reduction of Ru^{3+} in the outer layer by Fe^{2+} in the inner layer.

Pt/$[Ru(vbpy)_3]^{2+}$/$[Fe(4,4'-(CH_2Br)_2bpy)_3]^{2+}$. A layer of polymerized $[Ru(vbpy)_3]^{2+}$ ($\Gamma = 7.6 \times 10^{-9}$ mol/cm^2) was formed by reductive electropolymerization. In a second step a layer of electropolymerized $[Fe(4,4'-(CH_2Br)_2bpy)_3]^{2+}$ was added. In Figure 7C is shown a cyclic voltammogram of the resulting bilayer film. The sharp prepeak observed at the onset of the oxidative component for the $Ru^{III/II}$ couple is a consequence of the bilayer structure. The outer layer, which contains Fe^{2+}, is isolated from the electrode. Oxidation of Fe^{2+} requires mediation by the Ru^{3+} sites in the inner layer. Reductive components for both the $Ru^{III/II}$ and $Fe^{III/II}$ couples are observed on the return scan. The reduction of Fe^{3+} to Fe^{2+} occurs because of the large overlap between the $Ru^{III/II}$ and $Fe^{III/II}$ waves.[18a] Fe^{3+} in the outer layer formed in the oxidative scan cannot be trapped.

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Notes

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Photochemistry of Chlorochromium(III) Tetraphenylporphyrinate in Acetone. Studies on Photodissociation of the Axial Acetone in the Temperature Range 180–295 K by Laser Photolysis

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It is well-known that natural and synthetic metalloporphyrins undergo photodissociation of the axial ligand such as CO, NO, O_2, CN^-, or pyridine upon light irradiation. By means of pico- and nanosecond laser photolyses, many studies of the reactive state for the ligand dissociation as well as on deactivation processes of excited states have been carried out.[1] These studies help extensively to understand the effects of the axial ligand on the excited-state behavior of metalloporphyrins.

For chromium porphyrins, in our previous paper,[2] it was reported that the pyridinate of $ClCr^{III}(TPP)$, $ClCr^{III}(TPP)Py$ (Py = pyridine), in acetone photodissociates the axial pyridine to produce $ClCr^{III}(TPP)$ with a quantum yield of 0.16 upon both 355- and 532-nm laser irradiation at room temperature. Since no excitation wavelength dependence was observed, we had three candidates for the reactive state for dissociation: the triplet–sextet, $^6T_1$, the triplet–quartet, $^4T_1$, and the singlet–quartet, $^4S_1$, states.[3] On the basis of the following two reasons, neither the $^4T_1$ nor the $^6T_1$ state is the reactive state: (1) the quantum yields for photodissociation are independent of the concentrations of oxygen; (2) the $^6T_1$ state, which is in thermal equilibrium with the $^4T_1$ state, is quenched by oxygen. Therefore, the $^4S_1$ state wsa concluded to be the reactive state for the dissociation of Py from $ClCr^{III}(TPP)Py$.

In the present work, we have investigated the photochemistry of the photodissociation of the axial acetone from the acetonate of $ClCr^{III}(TPP)$, $ClCr^{III}(TPP)Ac$ (Ac = acetone), by laser pho-

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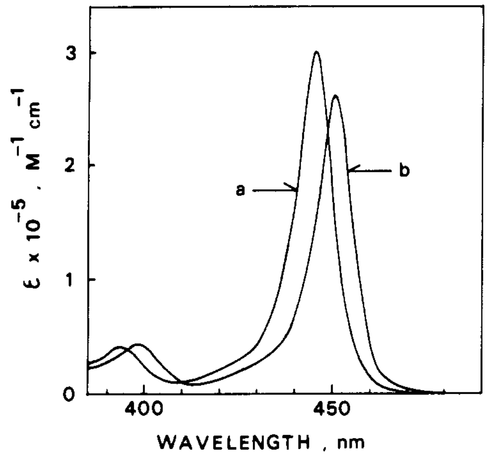

Figure 1. Absorption spectra of $ClCr^{III}(TPP)$ in (a) acetone and (b) CH_2Cl_2 at room temperature.

tolysis in the temperature range 180–295 K. On the basis of the quantum yield measurements of the photodissociation of Ac and the $^6T_1$ state at various temperatures, the reactive state for the dissociation of Ac from $ClCr^{III}(TPP)Ac$ as well as deactivation processes of the excited chromium(III) porphyrins is discussed in detail.

Experimental Section

$ClCr^{III}(TPP)$ was synthesized and purified according to the literature procedure.[4] Reagent grade acetone and dichloromethane were used as supplied.

Absorption and luminescence spectra were recorded on a Hitachi 330 spectrophotometer and a Hitachi MPF 4 fluorescence spectrophotometer, respectively. Laser photolysis studies were carried out by using the second (532 nm) and third harmonics (355 nm) of a Nd-YAG laser from J. K. Laser Ltd.: the pulse duration and energy were 20 ns and 100 mJ/pulse, respectively. The detection system used for observation of transient spectra has been described elsewhere.[5] Temperatures of sample solutions were controlled by a cryostat from Oxford Instruments (Model DN 10200) with a precision of ±1.0 °C.

Sample solutions were prepared in the dark to prevent photodecomposition of $ClCr^{III}(TPP)$ and were degassed to ca. 10^{-6} Torr on a vacuum line by freeze–pump–thaw cycles.

Results and Discussion

Figure 1 shows absorption spectra of $ClCr^{III}(TPP)$ in acetone and dichloromethane at room temperature. The molar absorption coefficients were determined as 3.0×10^5 M^{-1} cm^{-1} at 446 nm and 2.6×10^5 M^{-1} cm^{-1} at 451 nm in acetone and dichloromethane, respectively. Since CH_2Cl_2 is regarded as a noncoordinating solvent, the difference in the peak wavelength between these spectra indicates that, in an acetone solution, $ClCr^{III}(TPP)$ is coordinated with an acetone molecule, Ac, as the sixth ligand to form $ClCr^{III}(TPP)Ac$.

Figure 2 shows the transient spectra observed for a degassed acetone solution of $ClCr^{III}(TPP)Ac$ (4.02×10^{-6} M) at (a) 50 ns and (b) 2 μs after 355-nm laser pulsing at room temperature. Transient spectrum a decays within 200 ns, leaving transient spectrum b, which returns to the spectrum of $ClCr^{III}(TPP)Ac$ with the first-order rate constant $k_d = 5.7 \times 10^3$ s^{-1}. No residual absorption was observed after the decay of transient b. The fast decay component of the transient spectra obtained by subtracting transient spectrum b from transient spectrum a is ascribed to the $^6T_1$ state of $ClCr^{III}(TPP)Ac$.[2]

Transient spectrum b having the positive peak at 455 nm and the negative one at 445 nm is quite similar to the difference spectrum obtained by subtracting the spectrum of $ClCr^{III}(TPP)$ in CH_2Cl_2 from that in acetone. As described above, CH_2Cl_2 is regarded as a noncoordinating solvent. Thus, transient b is ascribed to $ClCr^{III}(TPP)$ having no axial acetone:

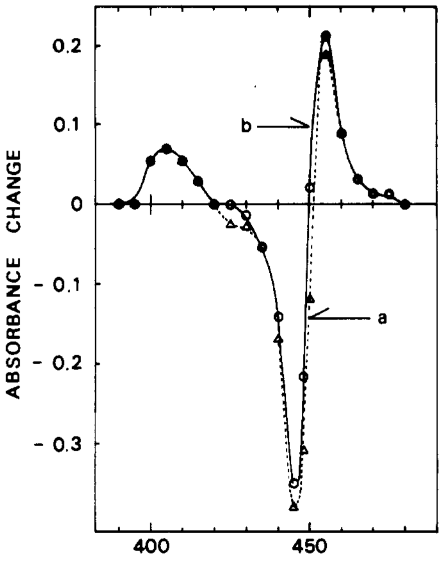

Figure 2. Transient spectra observed for an acetone solution of $ClCr^{III}(TPP)$ (4.02×10^{-6} M) after a 355-nm laser pulse at (a) 50 ns (Δ) and (b) 2 μs (○) at room temperature.

$$ClCr^{III}(TPP)Ac \xrightarrow{h\nu} {}^6T_1$$

$$ClCr^{III}(TPP)Ac \xrightarrow{h\nu} ClCr^{III}(TPP) + Ac$$

$$ClCr^{III}(TPP) + Ac \xrightarrow{k_d} ClCr^{III}(TPP)Ac$$

Photoexcitation of $ClCr^{III}(TPP)Ac$ gives the $^6T_1$ state and causes dissociation of the axial Ac to yield five-coordinated $ClCr^{III}(TPP)$, which recombines with Ac to regenerate $ClCr^{III}(TPP)Ac$ with the rate constant $k_d = k_{Ac}[Ac]$. The value of k_{Ac} was calculated as 4.2×10^2 M^{-1} s^{-1}. This value is in a good agreement with that obtained from the studies on photodissociation of $ClCr^{III}(TPP)Py$ in an acetone solution (4.2×10^2 M^{-1} s^{-1}).[2]

The quantum yield, ϕ_{dis}, for photodissociation of the axial acetone from $ClCr^{III}(TPP)Ac$ was determined with the laser photolysis technique. The number of photons absorbed by $ClCr^{III}(TPP)Ac$, I_{abs}, at a laser excitation wavelength (532 or 355 nm) was determined by measuring the triplet–triplet (T–T) absorption of zinc(II) tetraphenylporphyrinate, $Zn^{II}(TPP)$, in benzene. The triplet yield, ϕ_T, and the molar absorption coefficient, ϵ_{470}, at 470 nm of the triplet state of $Zn^{II}(TPP)$ have been reported as 0.83 and 7.3×10^4 M^{-1} cm^{-1}, respectively.[6] After laser pulsing, the initial absorbance change, ΔD_T, observed for formation of the triplet state of $Zn^{II}(TPP)$ is represented as

$$\Delta D_T = \phi_T \epsilon_{470} I_{abs} \tag{1}$$

On the other hand, when an acetone solution of $ClCr^{III}(TPP)Ac$ has the same absorbance at the irradiation wavelength as that of the benzene solution of $Zn^{II}(TPP)$ and is subjected to laser irradiation, the quantum yield, ϕ_{dis}, for photodissociation of Ac from $ClCr^{III}(TPP)Ac$ is expressed as

$$\phi_{dis} = \Delta D_{dis}(\Delta\epsilon)^{-1} I_{abs}^{-1} \tag{2}$$

Here, ΔD_{dis} and $\Delta\epsilon$ are the absorbance change at 445 nm observed at 2 μs after laser pulsing and the difference in the molar absorption coefficient at 445 nm between $ClCr^{III}(TPP)Ac$ in acetone and $ClCr^{III}(TPP)$ in CH_2Cl_2 (1.32×10^5 M^{-1} cm^{-1}). With the use of eq 1, eq 2 is transformed to

$$\phi_{dis} = \Delta D_{dis}(\Delta D_T)^{-1} \epsilon_{470} (\Delta\epsilon)^{-1} \phi_T \tag{3}$$

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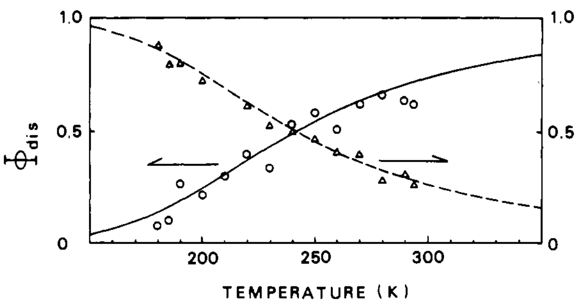

Figure 3. Plot of the quantum yields, ϕ_{dis}, for dissociation of the axial acetone (O) and the yields, ϕ_{TS}, of the $^6T_1$ state (Δ) in the temperature range 180–295 K. The solid and broken lines are the values calculated according to the reaction scheme (see text).

The quantum yields for photodissociation of the axial acetone at 295 K were determined as 0.63 ± 0.03 and 0.55 ± 0.05 upon 355- and 532-nm laser irradiation, respectively. These results reveal that the quantum yield for photodissociation of Ac has no excitation wavelength dependence within an experimental error. In agreement with the present case of $ClCr^{III}(TPP)Ac$, it is reported that the quantum yield for photodissociation of the axial pyridine from $ClCr^{III}(TPP)Py$ is independent of the irradiation wavelength.[2]

By the analogy to eq 2, the quantum yield for the formation of the $^6T_1$ state, ϕ_{TS}, is expressed with the use of the molar absorption coefficient of the $^6T_1$ state at 470 nm, ϵ_{TS}, and the absorbance change, ΔD_{TS}, at 470 nm originating from the formation of the $^6T_1$ state as follows:

$$\phi_{TS} = \Delta D_{TS}\epsilon_{TS}^{-1}I_{abs}^{-1} \tag{4}$$

However, because of the difficulty in determining the value of ϵ_{TS}, the value of ϕ_{TS} could not be obtained experimentally. Since the products that we observed upon irradiation of $ClCr^{III}(TPP)Ac$ were merely $ClCr^{III}(TPP)$ and the $^6T_1$ state at 295 K, we assumed the value of ϕ_{TS} at 295 K as follows:

$$\phi_{TS}(295) = 1 - \phi_{dis}(295) \tag{5}$$

where $\phi_{dis}(295)$ is the quantum yield (=0.63) for photodissociation at 295 K. From eq 5, we obtain $\phi_{TS}(295) = 0.37$.

In order to study the temperature dependence of ϕ_{dis} and ϕ_{TS}, laser photolysis studies were executed with a cryostat in the temperature range 180–295 K.

According to eqs 2 and 4, the values of ϕ_{dis} and ϕ_{TS} at lower temperatures than 295 K can be determined by measurement of the absorbance changes, $\Delta D_{dis}(T)$ and $\Delta D_{TS}(T)$, at a given temperature, T, respectively: the quantum yields, $\phi_{dis}(T)$ and $\phi_{TS}(T)$, at a given temperature, T, are respectively represented as

$$\phi_{dis}(T) = \Delta D_{dis}(T)\ \Delta D_{dis}(295)^{-1}\ \phi_{dis}(295) \tag{6}$$

$$\phi_{TS}(T) = \Delta D_{TS}(T)\ \Delta D_{TS}(295)^{-1}\ \phi_{TS}(295) \tag{7}$$

where $\Delta D_{dis}(295)$ and $\Delta D_{TS}(295)$ are the absorbance changes at 295 K. By using $\phi_{dis}(295)$ (=0.63) and $\phi_{TS}(295)$ (=0.37), eqs 6 and 7, we obtained the values of ϕ_{dis} and ϕ_{TS}, respectively, in the temperature range 180–295 K. In Figure 3, the obtained values of ϕ_{dis} and ϕ_{TS} are represented in the temperature range studied. It was found that, from high to low temperatures, the quantum yield, ϕ_{dis}, decreases while ϕ_{TS} increases. The increase in the values of ϕ_{dis} at higher temperatures implies that the activation energy, ΔE_d, is necessary for dissociation of the axial Ac.

In the previous study,[2] it was suggested that photodissociation of the axial pyridine from $ClCr^{III}(TPP)Py$ occurs from the $^4S_1$ state. Here, similarly, we assume that photodissociation of Ac from $ClCr^{III}(TPP)Ac$ takes place via the $^4S_1$ state. In order to explain the mechanism of the dissociative reaction, we have depicted an energy diagram and decay rate processes of $ClCr^{III}(TPP)Ac$ in the excited states in Figure 4.

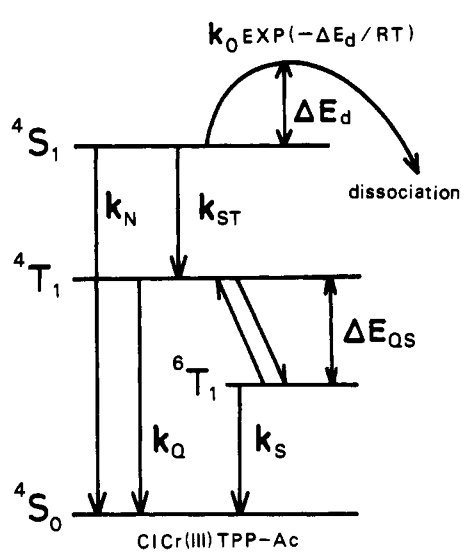

Figure 4. Energy scheme for the ground and the excited states of $ClCr^{III}(TPP)Ac$ (see text).

After excitation of $ClCr^{III}(TPP)Ac$ by laser irradiation, the $^4S_1$ state is produced within a duration of laser pulse. Besides the process for dissociation of Ac, the $^4S_1$ state deactivates to the ground state, $^4S_0$, and the $^4T_1$ states with the decay rate constants k_N and k_{ST}, respectively. Since no emission from the $^4S_1$ state is detected, k_N is considered to be a rate constant for nonradiative decay. At 295 K, the assumption of eq 5 implies $k_N = 0$. Below the $^4S_1$ state in energy, there are two excited states, $^4T_1$ and $^6T_1$. The energy level of the $^6T_1$ state is lower than that of the $^4T_1$ state. Between the $^4T_1$ and the $^6T_1$ states, Boltzmann distribution is assumed to be established with the energy gap, ΔE_{QS}.[3] The $^4T_1$ and the $^6T_1$ state decay to the $^4S_0$ state with the rate constants k_Q and k_S, respectively. On the assumption that the activation energy, ΔE_d, is necessary for dissociation, the rate constant k_{dis} for dissociation of Ac via the $^4S_1$ state at temperature T can be described by an Arrhenius expression with the frequency factor, k_0:

$$k_{dis} = k_0 \exp(-\Delta E_d/RT) \tag{8}$$

According to the energy scheme described above, the yield for dissociation, ϕ_{dis}, is formulated as follows:

$$\phi_{dis} = k_{dis}(k_N + k_{ST} + k_{dis})^{-1} \tag{9}$$

By use of eq 8, eq 9 can be rewritten as

$$\phi_{dis} = [1 + K \exp(\Delta E_d/RT)]^{-1} \tag{10}$$

where

$$K = (k_N + k_{ST})/k_0 \tag{11}$$

Equation 10 is transformed to

$$\ln (\phi_{dis}^{-1} - 1) = \ln K + \Delta E_d\ R^{-1}T^{-1} \tag{12}$$

for easier analysis. Plots of $\ln (\phi_{dis}^{-1} - 1)$ vs T^{-1} give a straight line. From the slope and the intercept of the line, we obtain

$$\Delta E_d = 2.6 \text{ kcal/mol} \tag{13}$$

$$K = (k_N + k_{ST})/k_0 = 4.7 \times 10^{-3} \tag{14}$$

The solid line in Figure 3 plots the values of ϕ_{dis} calculated with eqs 10, 13, and 14. Good agreement between the experimental values of $\phi_{dis}(T)$ and the solid line justifies the mechanism proposed for the dissociative process depicted in Figure 4.

With a decrease in temperature, the values of ϕ_{TS} tend to increase while those of ϕ_{dis} decrease. Concerning the values of ϕ_{TS} at lower temperatures, we assume that eq 5 holds not only at 295 K but also in the whole temperature range studied. This implies $k_N = 0$ independent of temperature. By use of eqs 5 and 10, ϕ_{TS} is represented as

$$\phi_{TS} = 1 - [1 + K \exp(\Delta E_d/RT)]^{-1} \tag{15}$$

The broken line in Figure 3 represents the values of ϕ_{TS} calculated from eq 15 and the values of ΔE_d and K shown in eqs 13 and 14, respectively. Because the experimental values of $\phi_{TS}(T)$ are in good accord with those calculated, we consider that $k_N = 0$ holds in the temperature range studied, as assumed above. It, therefore, is likely that the photoexcited ClCr^{III}(TPP)Ac is fated to undergo the dissociation of the axial acetone or result in the formation of the $^4T_1$ state.

When the $^4T_1$ state is formed, the $^6T_1$ state is populated, leading to establishment of Boltzmann equilibrium between the $^4T_1$ and $^6T_1$ states.[3] As will be mentioned later, the excited state detected by laser photolysis of ClCr^{III}(TPP)Ac is principally ascribed to the $^6T_1$ state. At room temperature, the lifetime of the $^6T_1$ state is too short, less than 100 ns, to determine precisely the decay rate constant by our laser system. However, laser photolysis at lower temperatures enables us to observe the decay profile of the transient spectrum of the $^6T_1$ state. In the temperature range 180–230 K, we could measure the decay rate constants of the $^6T_1$ state, k_{obsd}, represented as[3]

$$k_{obsd} = (k_S + \chi k_Q)(1 + \chi)^{-1} \qquad (16)$$

where

$$\chi = \tfrac{2}{3} \exp(-\Delta E_{QS}/RT) \qquad (17)$$

On the assumption $\chi \ll 1$, eq 16 will be transformed to

$$\ln (k_{obsd} - k_S) = \ln (\tfrac{2}{3}k_Q) - \Delta E_{QS}R^{-1}T^{-1} \qquad (18)$$

With the use of $k_S = 4.4 \times 10^5$ s^{-1}, the plot of ln ($k_{obsd} - k_S$) vs T^{-1} gave a straight line. From the slope and intercept of the line, we obtained the following values:

$$\Delta E_{QS} = 770 \text{ cm}^{-1} \qquad k_Q = 8.9 \times 10^8 \text{ s}^{-1}$$
$$k_S = 4.4 \times 10^5 \text{ s}^{-1}$$

Because the values of χ can be calculated with the obtained value of ΔE_{QS} (770 cm^{-1}) as $\chi = 10^{-3}$–$10^{-4} \ll 1$ in the temperature range 180–295 K, the assumption $\chi \ll 1$ used in derivation of eq 18 is appropriate. The value of χ stands for the ratio of the population of the $^4T_1$ state to that of the $^6T_1$ state. Thus, the observed excited state detected after laser irradiation of ClCr^{III}(TPP)Ac is concluded to be the $^6T_1$ state.

Gouterman et al.[3] reported the value of ΔE_{QS} as 520 cm^{-1} by measuring dual luminescence around 815 and 850 nm from the $^4T_1$ and $^6T_1$ states of ClCr^{III}(TPP), respectively, in a mixture of 1-butanol and 3-methylpentane in the wide temperature range 300–1.8 K. It was difficult for us to detect luminescence in an acetone solution of ClCr^{III}(TPP)Ac at room temperature. However, at 180 K, weak luminescence with a peak around 825 nm was clearly observed, which is probably from the $^4T_1$ state. From the luminescence peak of the $^4T_1$ state and the value of ΔE_{QS} = 770 cm^{-1}, luminescence from the $^6T_1$ state in acetone is expected to be observed at 880 nm. However, no luminescence from the $^6T_1$ state could be detected at temperatures higher than the freezing point of acetone (178 K). Below 180 K, we were unable to observe luminescence from an acetone solution because acetone is opaque below its freezing point.

Conclusion

The acetonate of ClCr^{III}(TPP), ClCr^{III}(TPP)Ac, photodissociates the axial ligand, Ac, via the $^4S_1$ state with a quantum yield of ca. 0.6 at 295 K independent of irradiation wavelength, 355 or 532 nm. The activation energy for the dissociation of Ac in the $^4S_1$ state is obtained as 2.6 kcal/mol.

From the quantum yield measurements for photodissociation of Ac and the formation of the $^4T_1$ state in the temperature range 180–295 K, it is revealed that no radiationless transition occurs from the $^4S_1$ state to the ground state.

The energy gap between the $^4T_1$ and $^6T_1$ states in acetone is evaluated as 770 cm^{-1} on the basis of measurements of the decay rate constants of the $^6T_1$ state in the temperature range 180–230 K.

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Reduction of BH$_3$·THF by Alkali Metal (K, Rb, Cs) and Ytterbium Mercury Amalgams To Form Salts of [B$_3$H$_8$]$^-$: A Simple Procedure for the Synthesis of Tetraborane(10)

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Received February 26, 1991

The octahydrotriborate(1−) ion, [B$_3$H$_8$]$^-$, is employed in a wide variety of applications: syntheses of novel metallaborane,[1] higher borane,[2] heteroatom borane,[3] and carborane cluster compounds;[4] the reduction of a wide variety of organic compounds;[5] the preparation of electrode coatings through reduction reactions;[6] applications to explosive and propellant technology;[7] neutron capture therapy;[8] and serum triglyceride and serum cholesterol biological studies.[9]

A number of procedures have been reported for the preparation of [B$_3$H$_8$]$^-$ salts.[10-15] Of these, the most common starting points involve the reaction of sodium borohydride with boron trifluoride etherate[16] or the reaction of sodium borohydride with iodine.[7] However, Na[B$_3$H$_8$] is highly solvated by the ether solvent in these reactions, making it difficult to measure, accurately, amounts of

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