on A and B, ϵ is the dielectric constant of the fluid, a is the distance of closest approach of A and B, and the other constants have their usual meanings.

(17) See, for example, C. H. Langford and J. P. H. Tong, *Acc. Chem. Res.*, **10**, 258 (1977).

(18) This ratio was calculated by use of the data given by Palmer and Harris[1] for the cis tetrachloro complex, by W. Robb and M. M. de V. Steyn, *Inorg. Chem.*, **6**, 616 (1969), for the pentachloro complex, and by W. Robb and G. M. Harris, *J. Am. Chem. Soc.*, **87**, 4472 (1965), for the hexachloro complex.

(19) K. E. Hyde, H. Kelm, and D. A. Palmer, *Inorg. Chem.*, **17**, 1647 (1978).

(20) S. A. Johnson, F. Basolo, and R. G. Pearson, *J. Am. Chem. Soc.* **85**, 1741 (1963).

(21) C. Bifano and R. G. Linck, *Inorg. Chem.*, **7**, 908 (1968).

Contribution from the Departments of Chemistry, Università di Perugia, 06100 Perugia, Italy,
and the State University of New York at Binghamton, Binghamton, New York 13901

Photochemical and Thermal Reactions of Tris(acetylacetonato)chromium(III) in Water-Ethanol Solution

EDOARDO ZINATO,* PIETRO RICCIERI, and PETER S. SHERIDAN

Received July 26, 1978

Irradiation of 50% v/v water-ethanol solutions of $Cr(acac)_3$ at 16 wavelengths between 230 and 730 nm leads to replacement of one acetylacetonate ligand by two water molecules. The photoproduct is cationic, neutral, or anionic depending on solution pH and was characterized by absorption spectra, chemical analysis, ion exchange, and conductivity. The photoaquation quantum yields are pH independent between pH 0 and pH 13, are wavelength independent between 350 and 730 nm, and are atypically low for a Cr(III) complex ($\phi \approx 0.01$). A fourfold increase in quantum yield is observed upon 250-nm excitation, with no evidence for redox processes. The system is photochromic, as photoinduced acetylacetonate labilization is opposed by thermal anation of acetylacetone, and photostationary states can occur. The results are interpreted in terms of two distinct reactive excited states: a relatively unreactive ligand field (LF) state and a higher energy ligand-localized (LL) state.

Introduction

The remarkable stability,[1] the well-characterized structural properties,[2] absorption[3] and emission[4] spectra, and the variety of electronic transitions make tris(acetylacetonato)chromium(III) especially interesting from a photochemical point of view.[5] Previous investigations of $Cr(acac)_3$ and of other, variously substituted, β-diketonatochromium(III) chelates have focused on photoisomerization[6,7] and on partial photoresolution.[8-12] These studies, however, have been performed in organic, noncoordinating media such as hexane,[6,7] benzene,[10] and chlorobenzene,[8,9,12] where only intramolecular processes (either twisting or bond rupture and recoordination) are possible.

An understanding of the photochemical behavior of $Cr(acac)_3$ in a coordinating solvent is important for a number of reasons. (i) The solvent is thought to play a crucial role in the photochemical reactivity of many Cr(III) complexes,[13] so studies in noncoordinating solvents exclude an important reactant. (ii) The exceptional inertness[1] and extensive π-electron system[1-3] of the acetylacetonato ligand introduce factors which are rather unusual in photochemical studies of chromium(III).[13] (iii) The diversity of the absorption spectrum gives access to several types of electronic excitation, corresponding to ligand field (LF), charge-transfer (CT), and ligand-localized (LL) transitions.[5] Selective irradiation may yield some insight into the relative photochemical importance of the different excited states involved. (iv) The photochemical reactivity of $Cr(acac)_3$ can then be compared to the patterns established for the β-diketonates of other first-row transition metals, such as iron(III),[14] cobalt(III),[15] nickel(II),[16] and copper(II).[17] To date only qualitative observations have been reported on the photolysis of three β-diketonatochromium(III) complexes in alcoholic solvents, and only upon 254 nm irradiation.[5,18]

Experimental Section

Materials. $Cr(acac)_3$ was prepared and recrystallized following a described procedure.[19] The principal maxima of its absorption spectrum in 50% v/v water-ethanol solution are observed at 730 (sh, ϵ 0.4), 558 (68), 413 (sh, 200), 390 (435), 383 (440), 332 (16 700), and 257 nm (12 200) (Figure 1), in agreement with literature values.[3] $[Co(NH_3)_5F](NO_3)_2$ was obtained by a standard method.[20] Other chemicals and solvents were of reagent grade.

Analytical Methods. Free acetylacetone was determined spectrophotometrically, by use of a 0.02 M solution of *o*-phenylenediamine in 1 M $HClO_4$.[21] To an aliquot of the reaction mixture an equal volume of the reagent solution was added, and the optical density was measured at 490 nm (ϵ 840) after at least 10 min. At this wavelength the absorbance of $Cr(acac)_3$ is relatively low (ϵ 20.5). Standardization plots were linear in the 10^{-3}-10^{-5} M range. The reproducibility was not affected by the presence of the complex, up to at least 1 h after mixing. When $Cr(acac)_3$ was photolyzed in the presence of $Co(NH_3)_5F^{2+}$, Co^{2+} was analyzed spectrophotometrically at 625 nm (ϵ 1850) by the thiocyanate-acetone method.[22]

Optical densities of solutions were measured with a Beckman DU, and absorption spectra were recorded with either a Beckman DB or Cary 17 spectrophotometer. A glass microelectrode (Schott Model U 9258/81) immersed in the spectrophotometer cell and an Orion 801 digital potentiometer were used for pH determination. Electrical conductivity was measured with a Halosis S-Au bridge. Ion-exchange studies were performed with 4 × 1 cm columns by use of either Sephadex SP-C25 cationic resin in the proton form or Amberlite IRA-900 anion exchanger in the hydroxide form. Columns were preconditioned with 50% v/v water-ethanol mixtures before the photoproduct solution was loaded. Elution was with 50% v/v water-ethanol, $HClO_4$, or NaOH solutions.

Procedures. The general photolysis apparatus has been described previously.[23] Light sources consisted of either a 500-W, high-pressure Xe lamp or a 200-W, high-pressure Hg lamp. Irradiation wavelengths were selected by means of either Baird Atomic interference filters, which gave bands of ca. 10-nm half-width, or a Baush & Lomb high-intensity grating monochromator. The 254-nm radiation was obtained by filtering the emission of a Minerallight UVSL-25 lamp through 2 cm of $CoSO_4$- and $NiSO_4$-saturated solution. Light intensities were about 2×10^{-8} and 2×10^{-9} einstein s^{-1}, respectively, and were either continuously monitored by a thermopile[23] or measured using the reineckate[24] and ferrioxalate[25] actinometers. The actual absorbed energy was determined as described elsewhere.[26]

Solutions of $Cr(acac)_3$ in 50% v/v water-ethanol were photolyzed in thermostatted, standard spectrophotometer cells under continuous magnetic stirring. Complex concentrations ranged from 10^{-2} M (for

* To whom correspondence should be addressed at Università di Perugia.

0020-1669/79/1318-0720$01.00/0 © 1979 American Chemical Society

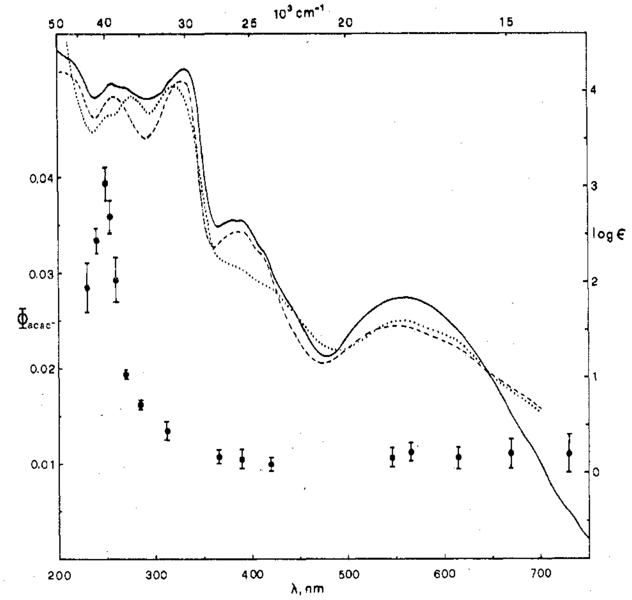

Figure 1. Absorption spectra in 50% v/v water–ethanol: solid line, $Cr(acac)_3$; broken lines, photoaquation product at pH 1 (---) and at pH 13 (···) (extinction coefficients on the right). The lower part of the figure shows wavelength dependence of photoaquation quantum yields (scale on the left).

irradiation of the long-wavelength, LF band) to 10^{-3} M (below 350 nm). Cell path lengths (1–10 cm) were such as to attain total light absorption. Some long-wavelength photolyses were performed on partially transmitting solutions.[23] The extent of reaction was always less than 10%, in order to minimize secondary photoprocesses, and thermal blank experiments were run during each photolysis. In a number of experiments, relatively large volumes of solution were exposed to continuous illumination under actinometric conditions. Aliquots were withdrawn at intervals (without interfering with the light beam) and were analyzed as above. The resulting volume changes were taken into account in evaluating quantum yields.

To study thermal reaction rates, hydroalcoholic solutions, 1×10^{-2} M in $Cr(acac)_3$, either freshly prepared or previously exposed to light, were brought to the desired temperature (±0.1 °C) in Al foil wrapped volumetric flasks. Aliquots (5 mL) were periodically cooled and analyzed. Rate constants were evaluated either as initial rates or by analyzing the approach to infinite-time concentrations (Results). The values obtained by the two methods agreed within experimental error. Average deviations were generally less than 10%. Activation enthalpies and entropies were derived from a least-squares analysis of log (k/T) vs. $1/T$.

Results

Water–ethanol solutions of tris(acetylacetonato)chromium(III) are very stable in the dark at room temperature: their absorption spectrum is not altered, and no free acetylacetone can be detected even after 10 days. Exposure to light of any wavelength between 615 and 230 nm causes a drop of the maximum of the low-energy (LF) absorption band and the occurrence of three isosbestic points at 645 (ε 13), 490 (21), and 443 nm (52). The spectral changes are accompanied by the appearance of uncoordinated acetylacetone and by an increase in solution conductivity. All of these changes are linearly related to the absorbed photon energy, through at least 6% conversion to photoproduct. If irradiated samples sit in the dark, the direction of the above changes is reversed and can be cycled many times by alternating irradiation and dark periods. At room temperature, the thermal back-reaction is slow (vide infra) and does not significantly affect analytical measurements upon photolysis.

The quantum yields for release of acetylacetone in 50% v/v water–ethanol, at 20 °C, using several excitation wavelengths are collected in Table I. At a given wavelength, the results are not changed, within experimental error, by increasing the ethanol concentration up to 80% v/v or by changing pH within the range pH 0 ($HClO_4$) and pH 13 (NaOH).

Table I. Quantum Yields for Acetylacetone Photoaquation of $Cr(acac)_3$ in 50% v/v Water–Ethanol Solution[a]

transition[b]	irradiation wavelength, nm	ϕ_{acac},[c] mol einstein^{-1}
$^4A_2 \rightarrow {}^2E$ (LF)	730 ± 10	0.011 ± 0.002 (3)
$^4A_2 \rightarrow {}^4T_2$ (LF)	670 ± 5	0.0110 ± 0.0015 (3)
	615 ± 5	0.0105 ± 0.0011 (3)
	565 ± 20	0.0112 ± 0.0009 (15)
	546 ± 5	0.0106 ± 0.0010 (16)
$^4T_2 \rightarrow {}^4T_1$ (LF)?	420 ± 10	0.0099 ± 0.0007 (13)
$t_{2g} \rightarrow \pi^*$ or $\pi \rightarrow e_g$ (CT)	390 ± 5	0.0105 ± 0.0010 (2)
	366 ± 5	0.0107 ± 0.0007 (15)
$\pi \rightarrow \pi^*$ (LL)	313 ± 4	0.0134 ± 0.0009 (7)
	285 ± 6	0.0161 ± 0.0002 (2)
	270 ± 7	0.0193 ± 0.0003 (2)
	260 ± 7	0.0293 ± 0.0028 (4)
	254 ± 4	0.0359 ± 0.0017 (11)
	250 ± 4	0.0393 ± 0.0018 (4)
	240 ± 7	0.0334 ± 0.0013 (4)
	230 ± 7	0.0285 ± 0.0027 (5)

[a] Room temperature of 18–22 °C. [b] Assignments are according to ref 5. LF states in O_h approximation. [c] Number of runs in parentheses.

The visible absorption spectrum of the photoproduced chromium(III) species was deduced by comparing the amounts of released β-diketone with the variations of optical density, recorded as expanded-scale difference spectra. On the assumption of photorelease of one bidentate ligand per complex molecule, the maximum at 560 nm was found to have an extinction coefficient of 35 ± 1 M^{-1} cm^{-1}.

The photoproduct was further characterized by ion-exchange experiments, as all of the chromium(III) species, present in solutions photolyzed to about 15% conversion, were completely eluted through cation- and anion-exchange resins by 50% v/v water–ethanol solutions. When irradiated samples were acidified to pH 2 ($HClO_4$), elution through the cationic exchanger with 2×10^{-2} M $HClO_4$ in 50% v/v water–ethanol removed only unreacted $Cr(acac)_3$ and free acetylacetone. The residual deep purple band was then totally displaced by 5×10^{-2} M $HClO_4$. In parallel experiments, this eluant displaced monopositive Cr(III) ions, such as $[Cr(NH_3)_4(C_2O_4)]^+$ and *trans*-$Cr(NH_3)_4Cl_2^+$, but not the dipositive ions $Cr(NH_3)_5Cl^{2+}$ and *trans*-$[Cr(NH_3)_4(H_2O)Cl]^{2+}$. Similar anion-exchange tests indicated that when the pH of the photolyzed solution was brought to ~13 (with NaOH), the photoproduct behaved as a monovalent anion.

The absorption spectra of the Cr(III) photoproduct, isolated at pH 2 and pH 13, are shown in Figure 1. Instantaneous interconversion between the two spectra occurs on changing pH, but neither the cation nor the anion could be separated from solution as a solid salt. The red shift of the long-wavelength (LF) band in alkaline solution is in agreement with the lower spectrochemical position of the OH^- ligand, relative to coordinated H_2O. The absorption features between 400 and 200 nm indicate acetylacetone ligands are still present in the primary coordination sphere of the photoproduct. Chromium determination of the eluates provided a quantitative characterization of the photoproduct spectra, confirming the independently measured extinction coefficient at 560 nm (vide supra). These observations clearly imply that the limiting forms $[Cr(acac)_2(H_2O)_2]^+$ and $[Cr(acac)_2(OH)_2]^-$ are predominant at low and high pH, respectively, while the neutral species, not retained by the resins at pH 8, is $[Cr(acac)_2(OH)(H_2O)]$.

Some irradiations at 254 (LL), 365 (CT), and 550 nm (LF) were carried out on oxygen-free (argon-saturated) solutions, in the presence of $Co(NH_3)_5F^{2+}$ as a potential scavenger for

Table II. Temperature Dependence of the Photochemical and Thermal Reactions of $Cr(acac)_3$ in 50% v/v Water–Ethanol Solution[a]

temp, °C	ϕ (λ 546 nm), mol einstein^{-1}	$10^7 k_1$(obsd), s^{-1}	$10^2 \times k_2$(obsd), M^{-1} s^{-1}	$10^4 [acac]_\infty$,[b] M
25.0	0.012 ± 0.001		1.3 ± 0.1	
35.0		0.21 ± 0.02	3.6 ± 0.2	0.97 ± 0.12
50.0	0.019 ± 0.002	1.6 ± 0.2	10.1 ± 1.2	1.82 ± 0.12
65.0	0.025 ± 0.002	8.6 ± 0.4	33 ± 1	3.27 ± 0.12
71.0	0.029 ± 0.002	17 ± 2		
$\Delta H^{\ddagger}$, kcal/mol	3.7 ± 0.1[c]	24.9 ± 0.3	15.2 ± 0.3	
$\Delta S^{\ddagger}$, eu		−13 ± 1	−16 ± 1	

[a] Average of at least three independent runs. [b] Concentration of uncoordinated acetylacetone, extrapolated to infinite time in the dark, in 10^{-2} M solutions of $Cr(acac)_3$. [c] Apparent activation energy.

Cr^{2+}.[27] No Co^{2+} was ever detected after photolysis. To the extent that such a test is diagnostic for the occurrence of primary photoredox processes, these results indicate that no Cr(II) species are formed, even upon UV excitation.

The photochemical reaction parallels the thermal aquation of the acetylacetonato ligand, as absorption changes for the photoreactions and dark reactions are identical; at room temperature, however, the rate of thermal aquation is negligible. At higher temperatures, the thermal forward reaction becomes more important and was found to follow pseudo-first-order kinetics (Table II).

The reverse process, thermal recombination of free acetylacetone and $[Cr(acac)_2(OH)(H_2O)]$, also occurs, as indicated by a decrease in free acetylacetone concentration and an increase in the LF band maximum at 560 nm, characteristic of $Cr(acac)_3$. Recombination in the dark (anation) does not proceed to completion, and a steady state of $Cr(acac)_3$, $[Cr(acac)_2(OH)(H_2O)]$, and acetylacetone is eventually established. The concentration of these species at the steady state is temperature dependent but is not dependent upon whether the steady state is approached by thermal aquation of $Cr(acac)_3$ or by anation of $[Cr(acac)_2(OH)(H_2O)]$ by free ligand. The thermal forward reaction (aquation) is several orders of magnitude slower than the thermal back reaction (anation), so the steady-state concentration of free diketone does not exceed a few percent, even at relatively high temperature (Table II).

The rates of ligand recoordination could be measured by following both the rise of the maximum at 560 nm and the disappearance of free acetylacetone. Spectral changes were small, so the latter method proved more precise and showed that a second-order rate law was obeyed through at least 60% conversion back to $Cr(acac)_3$. (Rate constants determined using spectral changes agreed with those determined by measuring free acetylacetone concentrations.) The anation rate constants were unaffected by the addition of free acetylacetone to the photolyzed solutions.

Despite the presence of parallel and competitive thermal processes, quantitative study of the photochemical aquation was possible. Under continuous irradiation at room temperature, the dark reactions are sufficiently slow that zero-order plots (photoproduct concentration graphed as a function of photolysis time) are linear through at least 6% photolysis (Figure 2). Upon prolonged photolysis, the thermal anation of photoproduct by free ligand becomes important, and the rate of photoinduced ligand release decreases. The effect of the back reaction is especially apparent at high temperature, where a photostationary state is generated. Photoaquation quantum yields, ϕ, upon irradiation at 546 nm (LF band excitation) were evaluated (1) from the initial slopes of zero-order plots (after subtracting the small contribution from thermal aquation) and (2) by fitting the observed photoproduct concentrations to the integrated form of eq 1, where k_1 and

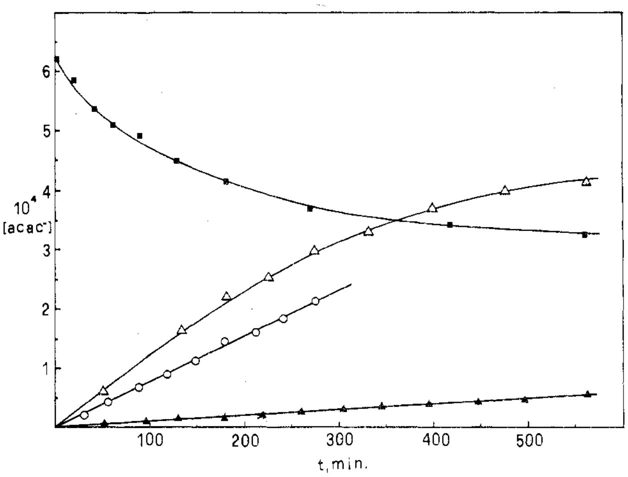

Figure 2. Photochemical and thermal reactions of 10^{-2} M $Cr(acac)_3$ in 50% v/v water–ethanol: ○, photoaquation at 25 °C ($I = 1.03 \times 10^{-6}$ einstein L^{-1} s^{-1}); △, photoaquation at 50 °C ($I = 1.08 \times 10^{-6}$ einstein L^{-1} s^{-1}); ▲, thermal aquation at 50 °C; ■, thermal recombination at 50 °C.

$$dx/dt = k_1(c - x) + I\phi - k_2x^2 \qquad (1)$$

k_2 denote the apparent first- and second-order rate constants for the forward and reverse dark reactions, respectively, I is the constant light intensity absorbed per unit volume, c is the zero-time concentration of $Cr(acac)_3$, and x is the instantaneous concentration of uncoordinated acetylacetone. The curve-fitting procedure was performed for photolyses done at several temperatures, and the temperature dependence of ϕ at 546 nm, k_1(obsd), and k_2(obsd) is summarized in Table II. The quantum yields determined from this more complete analysis agreed (±10%) with the values obtained from analysis of the initial slopes of the zero-order graphs (Figure 2).

The aquation of $Cr(acac)_3$ in 1–4 M $HClO_4$ solution has been reported elsewhere,[21] and a systematic investigation of the pH dependence of the thermal reactions was beyond the scope of this work, but scattered measurements indicated that thermal aquation is faster, and the steady-state concentration of free acetylacetone is higher at low or high pH than in neutral solution.

Discussion

The spectral, analytical, and kinetic results support the reaction scheme in eq 2 where XY = $(H_2O)_2$, $(H_2O)(OH)$,

$$Cr(acac)_3 + 2H_2O \underset{k_2}{\overset{\phi,\ k_1}{\rightleftharpoons}} [Cr(acac)_2XY]^z + acac(H) \qquad (2)$$

or $(OH)_2$, with z = 1+, 0, or 1−, respectively, depending on the solution pH. One β-diketone ligand is released in both the photoinduced and the thermal reactions, and it is assumed that water, not ethanol, is the solvating molecule. Various acid–base equilibria complicate any quantitative assessment of which species are present at different pH values, but qualitatively it is the buffering action of $[Cr(acac)_2(H_2O)_2]^+$ and Hacac which accounts for the rapid attainment of a constant pH of 8.2 during irradiation. At this pH, the predominant photoproducts are Hacac and $[Cr(acac)_2(OH)(H_2O)]$, but about 10% of the free ligand is in the deprotonated form (pK_a of Hacac ca. 9.0),[28] which accounts for the steady increase in the electrical conductivity during photolysis.

As expected on the basis of well-established models for Cr(III) photolysis,[13] LF excitation in the presence of a coordinating solvent leads to ligand substitution. The same reaction is observed upon irradiation in the ultraviolet, where absorbance is into CT and LL transitions. The lack of any observed redox photochemistry upon CT excitation is consistent with the behavior of other Cr(III) complexes but contrasts with all other first-row transition-metal β-diketonates,[5] which readily undergo photoinduced redox processes. Photoracemization[7] and photoresolution[8,9,12] of β-diketonato complexes of Cr(III) (in noncoordinating solvents) are generally inefficient ($\phi \approx 10^{-2}$), while non-β-diketonato Cr(III) complexes generally undergo efficient ligand photosubstitutions ($\phi \approx 0.1$–0.5). The quantum yields observed for the aquation of $Cr(acac)_3$ in water–ethanol solutions are of the same order of magnitude as those observed for the nonsubstitutional processes and are unusually low for photoinduced Cr(III) substitutions.

Any explanation of the relatively low efficiency of $Cr(acac)_3$ photolabilization will depend upon one (or both) of two general phenomena: (1) unusually rapid nonreactive deactivation of the excited state or (2) atypical chemical inertness of the photoreactive excited state. Collision with solvent molecules is a major deactivation route for excited-state species in room-temperature solution, yet the efficiency of photoinduced aquation of $Cr(acac)_3$ is remarkably independent of solvent–solvent cage structure; quantum yields are pH independent between pH 0 and pH 13 and are independent of the water/ethanol ratio (between 50/50 and 20/80) of the solvent.[29] In addition, $Cr(acac)_3$ is a neutral species and would not be expected to have the intimate solvent-shell characteristic of ionic species. Collision-induced deactivation to the ground state should not, therefore, be atypically rapid for excited states of $Cr(acac)_3$.

Among first-row transition-metal β-diketonates, the Cr(III) complexes are the only ones that exhibit phosphorescence ($^2E \rightarrow {}^4A_2$ in O_h approximation) in the visible region of the spectrum.[4] The lifetime of ^2E in rigid matrices at low temperature is in the range of those of normally photoreactive Cr(III) complexes.[4a,e,g] Although any quantitative extrapolation to room temperature (where $Cr(acac)_3$ does not emit) would be questionable, the suggestion is that under photolysis conditions photophysical deactivation processes may not be particularly unusual.

Hence, the photoinertness of $Cr(acac)_3$ may be essentially due to the unusual bonding of β-diketones to metals. Acetylacetone forms stable chelates with many transition metals,[1-3] and structural,[2] spectral,[3] and chemical[31] evidence suggests that orbitals of π symmetry are involved in extensive electron delocalization, and pseudoaromaticity, within the planar six-member chelate ring. This special bonding is clearly reflected in the chemical stability of the $Cr(acac)_3$ ground state. Even though Cr–O bonds are involved in both cases, thermal racemization[32] of $Cr(C_2O_4)_3^{3-}$ is faster, by several orders of magnitude, than similar processes in β-diketonate chelates,[7] and a factor of ca. 10^4 separates the aquation rates of $Cr(C_2O_4)_3^{3-}$ [33] and $Cr(acac)_3$. Formation of LF excited states would not significantly perturb the π delocalization which lends unusual stability to the ground state. The importance of π delocalization is also indicated by the lack of any evidence for one-ended coordinated diketone upon photolysis of $Cr(acac)_3$. It is likely that cleavage of one Cr–O bond is the primary photochemical process (associated with the σ-antibonding character of LF quartet excited states) but that destruction of the chelate ring also destroys the π conjugation, and rapid thermal aquation of the monodentate occurs.

The photochemistry of $Cr(acac)_3$ is characterized by two striking features: (1) the quantum yields for ligand labilization are pH insensitive and independent of excitation wavelength between 350 and 730 nm, and (2) a pronounced increase in photolabilization quantum yields occurs in a narrow region centered near 250 nm. The insensitivity of the quantum yields to pH changes indicates that protonation of the coordinated oxygen atoms, proposed as the first step in the thermal aquation in acidic solutions,[21] is not important in the reactivity of the photoproduced excited state.

Assignment of the absorption bands in the electronic spectrum of $Cr(acac)_3$ is hindered by the large number of possible transitions and the overlap between regions. While the assignment is not unambiguous, the ligand field (LF) region is generally considered to be between 350 and 750 nm, with charge-transfer (CT) excitation occurring between 400 and 200 nm.[5] The metal → ligand and ligand → metal CT transitions are thought to be almost degenerate, so assignment of the direction of charge transfer in any given band is not yet possible. The region between 200 and 300 nm contains some ligand localized (LL), $\pi \rightarrow \pi^*$ transitions[3,5] within the system of the chelate ring.

Wavelength independence has been observed for phosphorescence of β-diketonatochromium(III) complexes at 85 K upon 365-, 435-, and 546-nm excitation,[4a] for photoresolution between 365 and 650 nm,[8] and for photoisomerization at 350 and 577 nm.[7] Such a pattern parallels the present results and implies that there is virtually 100% efficient internal conversion between CT and LF states, as well as within the LF manifold, for Cr(III) β-diketonates.

Identification of the photoreactive state in Cr(III) has been the subject of much discussion.[13] The preeminence of the lowest quartet excited state has been generally established,[13] although evidence has recently been presented[34] for an ^2E photoreacting state in $Cr(bpy)_3^{3+}$. The thermal inertness of $Cr(acac)_3$ allowed accurate quantum yield determinations at 670 and 730 nm, where at least one-third of the absorbed energy directly populates the ^2E level. The quantum yields at these low-energy wavelengths are identical to those observed upon direct $^4T_2$ and CT excitation. Even though this constancy is compatible with a reactive doublet, alone it may be insufficient to distinguish between the two potentially reactive excited states. While at low temperatures the excitation energy is prevalently dissipated through phosphorescence from ^2E,[4] thermal equilibration between the ^2E and $^4T_2$ states may become possible at higher temperatures, following direct excitation to ^2E. Back ($^2E \rightarrow {}^4T_2$) intersystem crossing has been, in fact, recognized to be an important deactivation path for the doublet state even in complexes having larger Δ values than $Cr(acac)_3$.[35-38] A (thermally equilibrated) $^4T_2$–^2E energy gap of about 3×10^3 cm^{-1}, as estimated by an empirical procedure,[39] may not be large enough to exclude such an occurrence.

Despite the general observation of wavelength-independent photochemistry between 350 and 700 nm, only a few studies have dealt with the irradiation of tris(β-diketonato)chromium(III) complexes below 300 nm.[7a,18] A similar increase in quantum yields has been observed,[7a] however, as photoisomerizations of tris((+)-3-acetylcamphorato)chromium in hexane solutions were 2–5 times more efficient upon 254-nm excitation than upon 350- or 577-nm excitation.

The absorption bands between 200 and 300 nm are generally ascribed to ligand localized (LL), $\pi \rightarrow \pi^*$ transitions,[3,5] but there may be considerable mixing of CT and LL configurations in this region.[3g] The sharp maximum of the quantum-yield profile (Figure 1), corresponding to the 250-nm peak, provides evidence for the participation of two distinct reactive excited states. The inference is that (a) the 250-nm transition is orbitally different from those associated with the neighboring bands and (b) there is scarce communication between this state and the LF manifolds. In view of the absence of redox pathways around 250 nm, which are generally related to

CT-type excited states, and because of the fact that CT states of lower energy appear to efficiently convert to LF ones, the 257-nm band is suggested to be due to a $\pi \rightarrow \pi^*$, prevalently ligand-localized transition. The nearby absorption features (partially obscuring the tails of this band) may be attributed to CT-type transitions. Irradiation of the latter bands would be followed by efficient internal conversion to the low-lying, LF states, whereas the LL excitation would lead to the observed photosubstitution reaction through an excited-state mechanism different from that induced by LF irradiation. The promotion of one electron from a π to a π^* orbital would decrease the π bond order in the ring from 3 to 2, thus reducing the resistance to distortion away from the planar geometry of the ground state. Moreover, a $\pi \rightarrow \pi^*$ transition is expected to lower the electron density of the carbonyl oxygens, decreasing their coordinating ability. Cr–O bond cleavage and the observed photochemistry result.

When this study was completed, the involvement of two photoactive excited states was reported for another β-diketonatochromium(III) complex undergoing two different photoreactions in nonaqueous solvents.[40] In the 546–365-nm region, geometrical isomerization is either the main or the sole photolysis mode for *trans*-tris(1,1,1-trifluoropentane-2,4-dionato)chromium(III) with a low ($\sim 10^{-3}$) and virtually constant quantum yield. At 254 nm, photodecomposition becomes largely predominant over the former reaction, and the overall efficiency increases by one order of magnitude, showing a remarkable parallelism with the present quantum-yield pattern.

The photochemical behavior of $Cr(acac)_3$ is substantially different from that of other first-row transition-metal β-diketonates. Consistent with well-established patterns, excitation of either CT or LL bands leads to ligand substitution, characteristic of Cr(III) LF photochemistry. The Fe(III)[14] and Co(III)[15] tris(β-diketonates) exhibit no LF photochemistry, while redox processes result from irradiation of the CT bands. The wavelength dependence of quantum yields indicates that in $Cr(acac)_3$, high-energy CT states efficiently convert to lower energy LF states, while the LL state appears to display a distinctive photochemistry independent of either the CT or the LF states. For the other β-diketonates, redox decompositions dominate, and there is no evidence of a separate photochemistry resulting from the population of LL states, suggesting efficient internal conversion from LL to CT states in these complexes.[5]

Finally, the limited results on the thermal behavior of $Cr(acac)_3$ do not allow detailed mechanistic arguments, but the low aquation rate, compared to the rates observed for other Cr(III) complexes, certainly reflects the high stability of the chelate rings. Displacement of an acetylacetonato ligand is several orders of magnitude slower in water–ethanol solutions than in concentrated $HClO_4$ solutions.[21] In water–ethanol solutions, Cr–O bond fission would not be assisted by protonation of a coordinated oxygen, as proposed for the reactions at extremely low pH.

Facile recombination of the photoaquation products, as indicated by the high apparent rate constants and by the relatively low activation energy, again confirms the unusual stability of $Cr(acac)_3$.

Acknowledgment. Financial support from the National Research Council of Italy (CNR) and the National Science Foundation (Grant GP 27264) is gratefully acknowledged.

Registry No. $Cr(acac)_3$, 21679-31-2.

References and Notes

(1) J. P. Fackler, Jr., *Prog. Inorg. Chem.*, **7**, 361 (1966).
(2) E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88**, 2951 (1966).
(3) (a) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958); (b) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); (c) C. K. Jørgensen, *Acta Chem. Scand.*, **16**, 2406 (1962); (d) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **36**, 3330 (1962); (e) K. De Armond and L. S. Forster, *Spectrochim. Acta*, **18**, 1393 (1963); (f) P. X. Armendarez and L. S. Forster, *J. Chem. Phys.*, **40**, 273 (1964); (g) I. Hanazaki, F. Hanazaki, and S. Nagakura, *J. Chem. Phys.*, **50**, 276 (1969); (h) A. M. Fatta and R. L. Lintvedt, *Inorg. Chem.*, **10**, 478 (1971).
(4) (a) K. De Armond and L. S. Forster, *Spectrochim. Acta*, **19**, 1403, 1687 (1963); (b) H. L. Schläfer, H. Gausmann, and H. Witzke, *J. Chem. Phys.*, **46**, 1423 (1967); (c) S. N. Chen and G. B. Porter, *J. Am. Chem. Soc.*, **92**, 2189 (1970); (d) A. Pfeil, *J. Am. Chem. Soc.*, **93**, 5395 (1971); (e) J. T. Yardley and J. K. Beattie, *J. Am. Chem. Soc.*, **94**, 8925 (1972); (f) H. Otto, H. Yersin, and G. Gliemann, *Z. Phys. Chem. (Frankfurt am Main)*, **92**, 193 (1974); (g) W. M. Watson, Y. Wang, J. T. Yardley, and G. D. Stucky, *Inorg. Chem.*, **14**, 2374 (1975).
(5) R. L. Lintvedt in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Eds., Wiley, New York, 1975, Chapter 7, p 299.
(6) R. D. Koob, J. Beusen, S. Anderson, D. Gerber, S. P. Pappas, and M. L. Morris, *J. Chem. Soc., Chem. Commun.*, 966 (1972).
(7) (a) S. S. Minor and G. W. Everett, *Inorg. Chem.*, **15**, 1526 (1976); (b) *Inorg. Chim. Acta*, **20**, L51 (1976).
(8) K. L. Stevenson, *J. Am. Chem. Soc.*, **94**, 6652 (1972).
(9) K. L. Stevenson and T. P. vanden Driesche, *J. Am. Chem. Soc.*, **96**, 7964 (1974).
(10) H. Yoneda, U. Sakaguki, and Y. Nakashima, *Bull. Chem. Soc. Jpn.*, **48**, 1200 (1975).
(11) B. Norden, *Inorg. Nucl. Chem. Lett.*, **11**, 387 (1975).
(12) K. L. Stevenson and R. L. Baker, *Inorg. Chem.*, **15**, 1086 (1976).
(13) See for example E. Zinato in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Eds., Wiley, New York, 1975, Chapter 4, p 143.
(14) H. D. Gafney, R. L. Lintvedt, and S. Jaworiwsky, *Inorg. Chem.*, **9**, 1728 (1970).
(15) N. Filipescu and H. Way, *Inorg. Chem.*, **8**, 1863 (1969).
(16) H. D. Gafney and R. L. Lintvedt, *J. Am. Chem. Soc.*, **92**, 6996 (1970).
(17) H. D. Gafney and R. L. Lintvedt, *J. Am. Chem. Soc.*, **93**, 1623 (1971).
(18) H. D. Gafney, Ph.D. Thesis, Wayne State University, 1970.
(19) W. C. Fernelius and J. E. Blanch, *Inorg. Synth.*, **5**, 130 (1957).
(20) J. C. Bailar, Jr., *Inorg. Synth.*, **4**, 172 (1953).
(21) J. Aggett and A. L. Odell, *J. Chem. Soc. A*, 1820 (1966).
(22) R. E. Kitson, *Anal. Chem.*, **22**, 664 (1959).
(23) P. Riccieri and E. Zinato, *J. Am. Chem. Soc.*, **97**, 6071 (1975).
(24) E. E. Wegner and A. W. Adamson, *J. Am. Chem. Soc.*, **88**, 394 (1966).
(25) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(26) P. Riccieri and E. Zinato, *Z. Phys. Chem. (Frankfurt am Main)*, **79**, 28 (1972).
(27) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York, 1967.
(28) L. G. Sillēn and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17** (1964).
(29) Strong preferential solvation has been previously reported for $Cr(acac)_3$ in other solvents.[30] If excited-state $Cr(acac)_3$ should show a strong solvation preference for ethanol over water, this could also explain the solvent and pH independence of the photoreaction yields.
(30) L. S. Frankel, C. H. Langford, and T. R. Stengle, *J. Phys. Chem.*, **74**, 1376 (1970).
(31) J. P. Collman, R. A. Moss, H. Maltz, and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).
(32) S. T. Spees and A. W. Adamson, *Inorg. Chem.*, **1**, 53 (1962).
(33) K. U. Krishnamurty and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960).
(34) M. Maestri, F. Bolletta, L. Moggi, V. Balzani, M. S. Henry, and M. Z. Hoffman, *J. Chem. Soc., Chem. Commun.*, 491 (1977); *J. Am. Chem. Soc.*, **100**, 2694 (1978).
(35) G. B. Porter, S. N. Chen, H. L. Schläfer, and H. Gausmann, *Theor. Chim. Acta*, **20**, 81 (1971).
(36) N. A. P. Kane-Maguire and C. H. Langford, *J. Am. Chem. Soc.*, **94**, 2125 (1972).
(37) R. Ballardini, G. Varani, H. F. Wasgestian, L. Moggi, and V. Balzani, *J. Phys. Chem.*, 77, 2947 (1973).
(38) N. A. P. Kane-Maguire, D. E. Richardson, and C. B. Toney, *J. Am. Chem. Soc.*, **98**, 3996 (1976).
(39) P. D. Fleischauer, A. W. Adamson, and G. Sartori, *Prog. Inorg. Chem.*, **17**, 1 (1972).
(40) D. B. Yang and C. Kutal, *J. Chem. Soc., Chem. Commun.*, 363 (1978).