man[18,25] have been actively investigating the effect of mixed solvents on the decay kinetics of $[Cr(bpy)_3]^{3+}$. Although there is good agreement on a value of 63 μs for the lifetime of $[Cr(bpy)_3]^{3+}$ in pure, oxygen-free water,[10,18,25] there are differences between our data and theirs in mixed DMF–H_2O solutions.

We have previously noted[10] that in deaerated solutions, the luminescence lifetime and intensity of $[Cr(bpy)_3]^{3+}$ are both smaller by factor of 15 in neat DMF as compared to water. Henry and Hoffman found[18] that the ^2E-state absorption is easily measured in aqueous solution, but it is too weak to be detected in DMF. However, they also assert that the decay rate of the ^2E state is unchanged from water to $\chi_{DMF} = 0.1$. We find (see Figure 2) a large effect on the lifetime and phosphorescence intensity by small mole fractions of DMF such that, at $\chi_{DMF} = 0.1$, the lifetime has decreased from 63 μs in water to about half that value. In neat DMF $\tau = 4$ μs.

Figure 2 shows that the luminescence lifetime and intensity decrease in a parallel fashion as the mole fraction of DMF increases. All decays were strictly exponential. These data indicate that quenching by DMF must involve an increase in the rate of nonradiative decay of the ^2E state. The behavior cannot be rationalized in terms of variations in the population of the ^2E state due either to changes in the decay of the $^4T_2$ precursor or to changes in the efficiency of intersystem crossing to the ^2E state.

Concluding Remarks

The photochemistry of $[Cr(bpy)_3]^{3+}$ in DMF and the luminescence of the complex in mixed DMF–H_2O solutions have been investigated. We have observed that $[Cr(bpy)_3]^{2+}$ formed by photoreduction in neat DMF plays an important autocatalytic role in the decomposition of the substrate. In mixed DMF–H_2O systems, new, efficient nonradiative pathways become available for the decay of the ^2E state. The electron-transfer pathway in neat DMF probably does not play a significant kinetic role in the excited-state decay scheme; nevertheless this electron-transfer step is an important one since it is ultimately responsible for the formation of the trace amounts of $[Cr(bpy)_3]^{2+}$ involved in the catalysis. It is clear that the study of excited-state processes of $[Cr(bpy)_3]^{3+}$ in mixed-solvent systems is an area which is ripe for further careful investigation. Researchers in this area should pay particular attention to the role of dissolved oxygen.

Acknowledgment. Support of this work by the Natural Sciences and Engineering Council of Canada is gratefully acknowledged.

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Contribution from the Department of Chemistry, University of Georgia, Athens, Georgia 30602,
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Mechanistic Photochemistry of Transition-Metal β-Diketonate Complexes. 2.[1a] The Case of *trans*-Tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III)

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A detailed photochemical study of *trans*-$Cr(tfa)_3$ (tfa is the anion of 1,1,1-trifluoro-2,4-pentanedione) in several nonaqueous solvents is described. Both continuous and flash photolysis experiments reveal a more complex photoreactivity pattern than has heretofore been reported for chromium(III) β-diketonates. Trans to cis isomerization is the dominant process occurring upon irradiation at wavelengths ≥366 nm. Photolysis at 254 nm, on the other hand, results in both isomerization and redox decomposition, with the quantum efficiency of the latter pathway displaying a pronounced solvent dependence. The variation in the ratio of the quantum yields for the two processes with the excitation wavelength establishes the presence of two photoactive excited states in the complex. The lower energy state is assigned as the ligand field quartet, $^4T_{2g}$, whereas the higher lying state appears to contain appreciable ligand to metal charge-transfer character.

Introduction

Comparison of the reported photoreactivity patterns of first-row transition-metal β-diketonate complexes in nonaqueous solvents reveals an interesting dichotomy. Thus near-ultraviolet irradiation of the Mn(III),[2] Fe(III),[3] Co(III),[4] Ni(II),[5] and Cu(II)[6] complexes results in the one-electron reduction of the metal center by the ligand, whereas comparable excitation of the Cr(III)[7-9] analogues induces only stereochemical rearrangement. This apparent absence of a photoredox pathway in Cr(III) suggests that one or both of the following factors are operative. (i) The charge-transfer excited states of chromium(III) β-diketonates, though populated, are inherently unreactive in nonaqueous solvents. In other words, the principal relaxation pathways accessible to these excited states do not lead to redox products but instead terminate in the ground state of the original complex. (ii) The conditions under which past photochemical studies of chromium(III) β-diketonates were conducted tended to obscure any charge-transfer reactivity. This situation could obtain, for example, if the primary redox products undergo a rapid back-electron-transfer step to regenerate the parent complex.

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(1) (a) Part 1: Kutal, C.; Grutsch, P. A.; Ferraudi, G. *J. Am. Chem. Soc.* **1979**, *101*, 6884. (b) University of Georgia. (c) University of Notre Dame.

(2) Lintvedt, R. L. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P., Eds.; Wiley: New York, 1975; Chapter 7.

(3) Gafney, H. D.; Lintvedt, R. L.; Jaworiwsky, I. S. *Inorg. Chem.* **1970**, *9*, 1728.

(4) Filipescu, N.; Way, H. *Inorg. Chem.* **1969**, *8*, 1863.

(5) Gafney, H. D.; Lintvedt, R. L. *J. Am. Chem. Soc.* **1970**, *92*, 6996.

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(7) Koob, R. D.; Beusen, J.; Anderson, S.; Gerber, D.; Pappas, S. P.; Morris, M. L. *J. Chem. Soc., Chem. Commun.* **1972**, 966.

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(9) Minor, S. S.; Everett, G. W., Jr. *Inorg. Chem.* **1976**, *15*, 1526.

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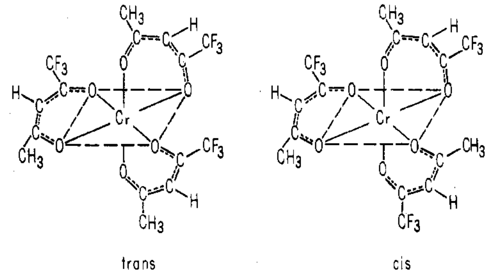

Figure 1. Structures of *trans*- and *cis*-Cr(tfa)$_3$.

With these possibilities in mind, we undertook a detailed photochemical investigation of *trans*-Cr(tfa)$_3$ (tfa is the anion of 1,1,1-trifluoro-2,4-pentanedione; see Figure 1) in several nonaqueous solvents. Both continuous and flash photolysis experiments have revealed that the photobehavior of this complex is considerably more diverse than that previously reported for chromium(III) β-diketonates. Particularly noteworthy is the observation of *two* photoinduced processes whose relative quantum efficiencies depend upon both the wavelength and the solvent. Moreover, we find evidence that one of these processes originates from an excited state containing appreciable charge-transfer character. A full account of our results, some of which have been communicated previously,[10,11] is presented here.

Experimental Section

a. Reagents. Cr(tfa)$_3$ was prepared and separated into trans and cis isomers by the procedure of Fay and Piper.[12] Anal. Calcd: C, 35.24; H, 2.36. Found for trans isomer: C, 35.30; H, 2.35. Tri-*n*-butylstannane was prepared by the method of van der Kerk et al.[13] and stored under nitrogen. Solvents employed in the spectral and photochemical studies were of at least reagent grade quality and were purified and dried by standard techniques.[14]

b. Continuous Photolysis Procedures. Photolyses at 254 nm were performed by using a Pen-Ray lamp (Ultraviolet Products).[15] Samples irradiated at this wavelength were degassed by three successive freeze–pump–thaw cycles. Higher wavelength irradiations on nondegassed samples were provided by a 200-W high-pressure mercury-arc lamp (Illumination Industries) in conjunction with appropriate blocking and interference filters for monochromatization. Light intensity was determined by ferrioxalate[16] or Reineckate[17] actinometry.

Photolyzed solutions were analyzed by gas chromatography using a Varian Model 1440 gas chromatograph equipped with a scandium tritide electron-capture detector. The operating temperatures of the instrument were as follows: injector port, 140 °C; column 92 °C; detector, 140 °C. Separation of trans–cis isomers was accomplished on a 12-in. glass column (4-mm i.d.) containing open-pore polyurethane.[18] The flow rate of nitrogen carrier gas was 30 mL/min. Since the electron-capture detector exhibited a 1:1 response factor for the two isomers, the ratio of peak areas (determined by planimetry) represents a direct measure of the extent of isomerization. Decomposition was monitored by comparing the total (trans + cis) peak area of an irradiated sample with that of an unirradiated standard.

Electronic absorption spectra were measured by using a Cary 15 spectrophotometer. Identification of free H(tfa) as a photoproduct was accomplished by trap to trap distillation of the photolyzed solution followed by comparison of the absorption spectrum of the distillate to that of an authentic sample of the ligand.

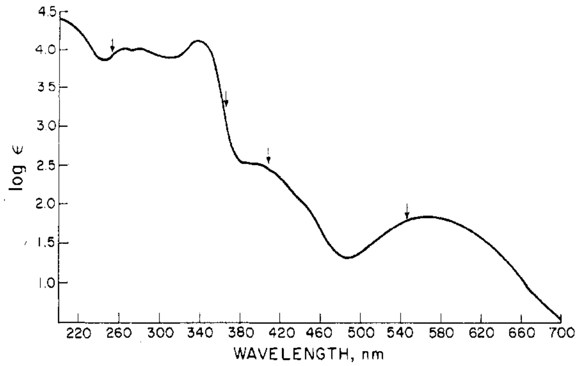

Figure 2. Electronic absorption spectrum of *trans*-Cr(tfa)$_3$ in ethanol. Arrows indicate irradiation wavelengths in continuous photolysis studies.

c. Flash Photolysis Procedures. Sample solutions were prepared by dissolving *trans*-Cr(tfa)$_3$ in solvents which had been deaerated by bubbling with argon. All additional manipulations were carried out under an argon atmosphere in a gastight apparatus.

Flash irradiations were performed by using an apparatus described previously.[19] Pulses of polychromatic light ($\geq$240 nm) of $\sim$30-μs half-life were obtained for stored electrical energies between 60 and 250 J/flash. Cutoff filters placed in the path of the exciting light were used to isolate different spectral regions. The results of time-resolved optical detection were analyzed by already reported methods.[19,20]

Results and Discussion

a. Spectral Assignments. The spectral characteristics of tris(β-diketonato)chromium(III) complexes vary somewhat with the nature of the substituents located on the ligands,[21,22] but in general, ligand field, metal–ligand charge-transfer, and ligand-localized excited states are all accessible to light in the visible and near-ultraviolet wavelength regions. This richness of excited states complicates the task of assigning transitions, particularly when two or more absorption bands overlap. The occurrence of configuration mixing between states of identical symmetry and comparable energies further exacerbates the situation, since in such cases the actual excited states reached via light absorption are of *mixed* orbital character and possess energies which may be shifted substantially from those predicted for the parent (unmixed) set. In view of these potential complications, it is perhaps not surprising that some uncertainty still attends the assignment of transitions in chromium(III) β-diketonates. In the remainder of the section we summarize and, where appropriate, appraise the validity of the various assignments which have been proposed for *trans*-Cr(tfa)$_3$.

The electronic absorption spectrum of *trans*-Cr(tfa)$_3$ in ethanol is reproduced in Figure 2. The broad band whose maximum lies at 568 nm is generally accepted to be the first spin-allowed ligand field transition, ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (labels refer to O_h symmetry). Though somewhat less certain, the second spin-allowed ligand field transition, ${}^4A_{2g} \rightarrow {}^4T_{1g}$ (F), is probably responsible for the slight shoulder appearing at $\sim$450 nm.[22] Fatta and Lintvedt[22] attribute the band at 390 nm to a charge-transfer transition, though they noted that no distinction can be made between ligand to metal or metal to ligand charge transfer on energetic grounds. In contrast, the single-crystal spectral analysis of Carlin and Piper[23] and the molecular orbital calculations of Nakagura and co-workers[24] on the closely related complex Cr(acac)$_3$ (acac is the anion

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(10) Yang, D. B.; Kutal, C. *J. Chem. Soc., Chem. Commun.* **1978**, 363.

(11) Ferraudi, G.; Yang, D. B.; Kutal, C. *J. Chem. Soc., Chem. Commun.* **1979**, 1050.

(12) Fay, R. C.; Piper, T. S. *J. Am. Chem. Soc.* **1963**, *85*, 500.

(13) Van der Kerk, G. J. M.; Noltes, J. G.; Luijten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 366.

(14) Riddick, J. A.; Bunger, W. B. "Organic Solvents", 3rd ed.; Wiley: New York, 1971.

(15) The lamp delivers 92% of its output at 254 nm. Quantum yields determined at this wavelength have been corrected accordingly.

(16) Hatchard, C. G.; Parker, C. A. *Proc. R. Soc. London, Ser. A* **1956**, *235*, 518.

(17) Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

(18) Kutal, C.; Sievers, R. E. *Inorg. Chem.* **1974**, *13*, 897.

(19) Ferraudi, G.; *Inorg. Chem.* **1978**, *17*, 1741.

(20) Ferraudi, G.; Endicott, J. F. *Inorg. Chem.* **1977**, *16*, 2762.

(21) DeArmond, K.; Forster, L. S. *Spectrochim. Acta* **1963**, *19*, 1393.

(22) Fatta, A. M.; Lintvedt, R. L. *Inorg. Chem.* **1971**, *10*, 478.

(23) Piper, T. S.; Carlin, R. L. *J. Chem. Phys.* **1962**, *36*, 3330.

(24) Hanazaki, I.; Hanazaki, F.; Nakagura, S. *J. Chem. Phys.* **1969**, *50*, 276.

of 2,4-pentanedione) suggest that this band arises from a spin-forbidden ligand-localized transition (n–π^* or π–π^*). The disparity between these assignments may be more apparent than real, however, since the latter two studies do not completely discount the possibility of some configurational mixing between ligand-localized and charge-transfer excited states. A charge-transfer assignment has been suggested[22] for the band occurring at 341 nm, but here again the direction of electron flow between the metal and ligand is uncertain. Higher energy bands, most notably those at 278 and 264 nm, have generally been ascribed to ligand-localized π–π^* transitions.[21,22] Molecular orbital calculations performed on Cr(acac)$_3$,[24] however, suggest that some charge-transfer character may also be involved.

Despite the uncertainty in assigning some of the electronic transitions in *trans*-Cr(tfa)$_3$, two points relevant to the photochemical behavior (vide infra) of the complex emerge from the preceding discussion. The first relates to the consequences of populating several different types (ligand field, charge transfer, ligand localized) of excited states. Recent work by Watts et al.[25,26] suggests that there is a tendency toward retention of orbital parentage during radiationless transitions between electronic states. This factor should therefore be conducive to wavelength-dependent photochemistry to the extent that reaction from a particular state becomes more competitive with relaxation pathways leading to lower lying states of different orbital character. Second, the existence of charge-transfer states at <400 nm and particularly <350 nm suggests that photoredox behavior in *trans*-Cr(tfa)$_3$ should become increasingly probable at shorter wavelengths of irradiation.

b. Continuous Photolysis Studies. The photochemical behavior of *trans*-Cr(tfa)$_3$ in several nonaqueous solvents is summarized in Table I. Trans to cis (see Figure 1) isomerization with essentially wavelength-independent quantum efficiency is the sole detectable process in benzene and cyclohexane upon irradiation at wavelengths ≥ 366 nm.[27] More complicated behavior obtains in 2-propanol and ethanol in that *both* isomerization and decomposition of the complex occur at 366 nm. The latter pathway assumes major importance in cyclohexane and alcoholic solvents upon 254-nm excitation as evidenced by the sharp rises in both the absolute magnitude of ϕ_{dec} and the quantum yield ratio, $\phi_{\mathrm{dec}}/\phi_{\mathrm{isom}}$. Analysis of the 254-nm photolyte in each case reveals the presence of free H(tfa).

Several experiments were performed to test the effects of various additives on the two photoinduced processes. We find that the 546-nm value of ϕ_{isom} measured in pure ethanol is unchanged upon addition of oxygen (i.e., air-saturating the solution)[28] or a 10-fold excess (relative to the *trans*-Cr(tfa)$_3$ concentration) of NH_4Cl or H_2SO_4. Likewise, the presence of a 10-fold excess of LiCl or H_2SO_4 has no discernible effect upon the 254-nm photochemistry in this solvent. In contrast, a 13-fold excess of the potent hydrogen atom donor tri-*n*-butylstannane[29] trebles the 254-nm value of ϕ_{dec} in cyclohexane, while the corresponding ϕ_{isom} value experiences a moderate reduction (Table I).

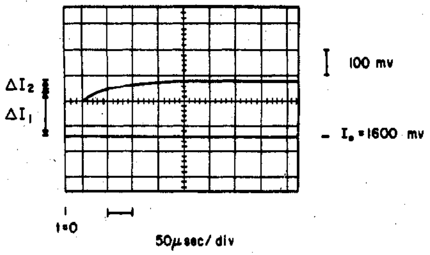

Figure 3. Oscillographic trace obtained upon flash photolysis of *trans*-Cr(tfa)$_3$ in a 40% 2-propanol in cyclohexane solution. The prompt (ΔI_1) and slow (ΔI_2) rises in the phototube voltage can be expressed as absorbance changes by employing the expression $\Delta A = -\log ((I_0 - \Delta I)/I_0)$, where I_0 is the pretrigger voltage.

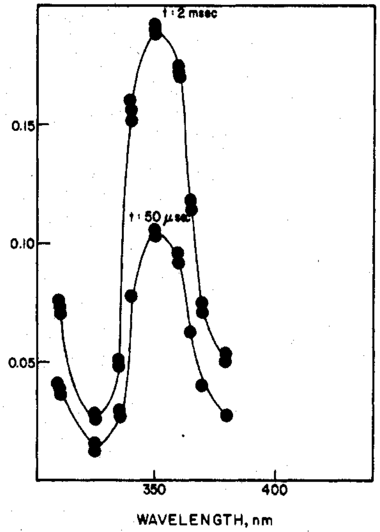

Figure 4. Spectra observed at various times following flash photolysis of *trans*-Cr(tfa)$_3$ in 2-propanol. The flash energy was 250 J.

Qualitatively similar spectral changes are observed upon 254-nm irradiation of *trans*-Cr(tfa)$_3$ in ethanol and 2-propanol. Thus the 341-nm band in the complex steadily decreases in intensity and shifts toward shorter wavelengths, while at short irradiation times, a new band (most likely due to free H(tfa)) grows in at ~280 nm. Upon continued irradiation, however, the latter feature begins to disappear. This behavior, coupled with the inability to maintain isosbestic points, attests to the increasing importance with time of one or more secondary photolysis processes. For minimization of the complications arising from this source, the quantum yields reported in Table I were determined at <10% reaction.

c. Flash Photolysis Studies. Flash photolysis of *trans*-Cr(tfa)$_3$ in deaerated alcohol–cyclohexane solvents induces a prompt (i.e., within the flash lifetime) increase in absorbance followed by a further slow growth at longer times (Figure 3). By employing cutoff filters to isolate specific spectral regions, we can establish that this behavior results from excitation with wavelengths ≤ 330 nm. The differential absorption spectra determined 50 μs and 2 ms after the flash are identical (Figure 4), indicating that the absorbance changes arise from a *single* reaction product, X. Moreover, the complex time dependence of the formation of X suggests that this species is generated from *trans*-Cr(tfa)$_3$ in consecutive photochemical (fast) and thermal (slow) steps (vide infra).

The absorbance change, ΔA_∞, at infinite time (generally >1 ms) after the flash is a direct measure of the total amount of X produced. As seen in Table II, this yield of X increases as a function of solvent in the order cyclohexane < ethanol < 2-propanol.

While X persists for relatively long periods (>10 s) in deaerated solutions, it reacts rapidly with several oxidants including oxygen and ferric ion. We infer from such behavior that X is a reducing species. Table III contains a compilation

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(25) Watts, R. J.; Brown, M. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1975**, *97*, 6029.

(26) Watts, R. J.; Griffith, B. G.; Harrington, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 674.

(27) Our 546-nm value of ϕ_{isom} in benzene is in fair agreement with a previously reported value measured in chlorobenzene: Stevenson, K. L.; vanden Driesche, T. P. *J. Am. Chem. Soc.* **1974**, *96*, 7964.

(28) Oxygen also has no discernible effect on the 546-nm value of ϕ_{isom} measured in benzene.

(29) Trotter, W.; Testa, A. C. *J. Am. Chem. Soc.* **1968**, *90*, 7044.

Table I. Quantum Yields for the Isomerization and Decomposition of *trans*-Cr(tfa)$_3$ upon Continuous Photolysis

wavelength irradiated, nm	benzene		cyclohexane		2-propanol		ethanol	
	$10^4\phi_{isom}$	ϕ_{dec}	ϕ_{isom}	ϕ_{dec}	$10^3\phi_{isom}$	ϕ_{dec}	$10^3\phi_{isom}$	ϕ_{dec}
546	6.7 ± 0.6	$<1 \times 10^{-4}$	-[a]	-	-	-	1.8 ± 0.03	$<1 \times 10^{-4}$
408	8.1 ± 1.1	$<2 \times 10^{-5}$	-	-	1.4 ± 0.04	$<1 \times 10^{-4}$	2.1 ± 0.1	$<1 \times 10^{-4}$
366	9.0 ± 0.2	$<2 \times 10^{-4}$	$(8.8 \pm 0.7) \times 10^{-4}$	$<6 \times 10^{-6}$	1.5 ± 0.1	$(2.8 \pm 0.5) \times 10^{-4}$	1.7 ± 0.2	$(2.3 \pm 0.2) \times 10^{-4}$
254[b]	-	-	$(3.2 \pm 0.1) \times 10^{-3}$	$(2.2 \pm 0.1) \times 10^{-3}$	2.4 ± 0.1	$(2.4 \pm 0.1) \times 10^{-2}$	4.4 ± 0.2	$(1.0 \pm 0.003) \times 10^{-2}$
			$(2.3 \pm 0.1) \times 10^{-3}$ [c]	$(6.6 \pm 0.4) \times 10^{-3}$ [c]				

[a] A dash indicates that no data were taken under the stated conditions. [b] Solutions irradiated at 254 nm were degassed by three freeze-thaw cycles. [c] Solution contains a 13-fold excess of HSn(n-Bu)$_3$.

Table II. Total Yield (ΔA_∞) of the Product, X, Observed in Flash Photolysis of *trans*-Cr(tfa)$_3$

ΔA_∞[a]	solvent	flash energy,[b] J/pulse
0.008	cyclohexane	250
0.11	ethanol	250
0.072	40% 2-propanol in cyclohexane	250
0.19	2-propanol	250
0.092	2-propanol	120
0.053	2-propanol	62

[a] Absorbance change at infinite time (>1 ms after the flash); average of at least five determinations at the 350-nm monitoring wavelength. [b] Deaerated solutions; [Cr(tfa)$_3$] = 7.5×10^{-5} M.

Table III. Pseudo-First-Order Rate Constants, k_{obsd}, for the Disappearance of the Product, X, Generated in the Flash Photolysis of *trans*-Cr(tfa)$_3$

k_{obsd},[a] s^{-1}	reaction conditions[b]	k_{obsd},[a] s^{-1}	reaction conditions[b]
<0.07	Ar bubbled	0.70	1×10^{-4} M Fe(ClO$_4$)$_3$
0.80	5×10^{-4} M O$_2$	1.5	2×10^{-4} M Fe(ClO$_4$)$_3$
1.7	1×10^{-3} M O$_2$	2.0	3×10^{-4} M Fe(ClO$_4$)$_3$

[a] Average of three to five determinations. [b] Studies were conducted at room temperature (25 ± 2 °C) and with 2-propanol.

of pseudo-first-order rate constants, k_{obsd}, characterizing the disappearance of X in the presence of large excesses of oxidant. Dividing k_{obsd} by the oxidant concentration yields the corresponding second-order rate constants, $k_{O_2} = 1.6 \times 10^3$ M^{-1} s^{-1} and $k_{Fe^{3+}} = 6.9 \times 10^3$ M^{-1} s^{-1}.

d. Mechanistic Considerations. Several mechanistic insights emerge from the continuous photolysis studies of *trans*-Cr(tfa)$_3$ summarized in Table I. The wavelength dependence of the quantum yield ratio, ϕ_{dec}/ϕ_{isom}, deserves special note, since such behavior establishes the presence of at least two photoactive excited states in the complex. We identify the state responsible for isomerization at longer wavelengths as the ligand field quartet, $^4T_{2g}$, on grounds that isomerization is heavily favored upon direct irradiation (546-nm light) into the $^4A_{2g} \rightarrow {}^4T_{2g}$ band.[30] Moreover, the constancy of ϕ_{isom} between 546 and 366 nm indicates that higher lying excited states in this interval undergo relaxation to $^4T_{2g}$ with near unit efficiency.

The characteristics of the $^4T_{2g}$ state in Cr(III) which enhance its reactivity relative to the ground state have been delineated previously.[31] For the present discussion we need only recall that the presence of an electron in a strongly σ-antibonding orbital weakens the metal–ligand bonding and can result in appreciable distortion of the molecular skeleton from its ground-state geometry. While the $^4T_{2g}$ state of tris(β-diketonato)chromium(III) complexes should thus be favorably disposed toward rearrangement, the detailed mechanism of this process has remained elusive. Both bond rupture and twisting pathways[32] have been proposed, but recent attempts[9,27] to distinguish between the two have resulted in the conclusion that both are probably operative. Though the present study does not resolve this question, the finding that ϕ_{isom} is relatively insensitive to changes in solvent polarity, ionic strength, and pH suggests that *trans*-Cr(tfa)$_3$ undergoes neither appreciable charge separation nor generation of a basic site during the course of photoinduced isomerization.

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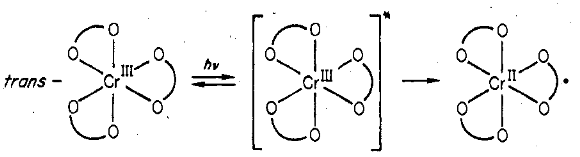
(30) The alternate possibility that isomerization originates from the low-lying ^2E_g state, populated via intersystem crossing from $^4T_{2g}$, seems less likely owing to the absence of significant distortion of the doublet from ground-state geometry.[31]

(31) Zinato, E. In "Concepts of Inorganic Photochemistry"; Adamson, A. W., Fleischauer, P., Eds.; Wiley: New York, 1975; Chapter 4.

(32) For a discussion of these rearrangement mechanisms see: Fortman, J. J.; Sievers, R. E. *Coord. Chem. Rev.* **1971**, *6*, 331.

We attribute the increasing importance of decomposition at excitation wavelengths ≤ 366 nm (Table I) to the population of a second, higher energy photoactive excited state which favors this pathway. The magnitude of ϕ_{dec} at 254 nm correlates reasonably well with the expected hydrogen atom donor ability of the solvent;[29,33] thus ϕ_{dec} increases in the order cyclohexane < ethanol < 2-propanol and cyclohexane < cyclohexane–$HSn(n\text{-}Bu)_3$. Such behavior clearly implicates hydrogen atom donation from the solvent as a key step in the mechanism of decomposition of *trans*-$Cr(tfa)_3$. Consideration of the flash photolysis data (Table II) reveals that the total yield of the reducing species, X, exhibits wavelength and solvent responses which parallel those of ϕ_{dec}. This close correspondence suggests that production of X and decomposition of the complex are related processes originating from the *same* excited state.

The main features of the photochemical behavior of *trans*-$Cr(tfa)_3$ upon irradiation at ≤ 366 nm agree well with a mechanism (reactions 1–3) in which the photoactive excited state possesses appreciable ligand to metal charge-transfer character. The redistribution of electron density that attends the population of this state generates a species, **1**, which formally contains Cr(II) bound to a β-diketone radical (reaction 1). In subsequent steps **1** may partition between two competing paths: (i) back electron transfer (reaction 2) to the ligand with regeneration of the parent trans complex (a portion of the time, however, this process is preceded by stereochemical rearrangement of **1** as evidenced by the rise in ϕ_{isom} between 366 and 254 nm (Table I)); (ii) hydrogen atom abstraction from the solvent (shown as 2-propanol) leading to the production of free H(tfa) and a solvated Cr(II) complex, **2** (reaction 3).[34] Path i is favored ($\phi_{isom} > \phi_{dec}$) in poor hydrogen atom donor solvents, whereas the opposite holds true for path ii.



(1)

1

$$\mathbf{1} \rightarrow trans\text{- or } cis\text{-}Cr(tfa)_3 \qquad (2)$$

$$\mathbf{1} + (CH_3)_2CHOH \rightarrow \underset{\mathbf{2}}{Cr(tfa)_2} + H(tfa) + (CH_3)_2\dot{C}OH \qquad (3)$$

We identify **2** as the metastable species X observed in flash photolysis. This assignment is in accord with the reducing properties exhibited by X (Table III); moreover, it accommodates the parallel wavelength and solvent responses of ϕ_{dec} and ΔA_{∞}. The prompt rise in absorbance (Figure 3) induced by the flash corresponds to the generation of **2** via reactions 1–3, whereas the slow growth observed at longer times arises from the additional production of **2** via secondary thermal reactions. A detailed analysis of these latter processes appears in the Appendix.

e. Concluding Remarks. The detection of a moderately efficient photoredox pathway in *trans*-$Cr(tfa)_3$ represents the first evidence that the ultraviolet photochemistry of chromium(III) β-diketonates in nonaqueous solvents is qualitatively similar to that of other first-row transition-metal β-diketonate complexes. Furthermore, the correlation between ϕ_{dec} and the hydrogen atom donor ability of the solvent (Table I) provides a basis for understanding the apparent absence of redox behavior in earlier photochemical studies[7,9] of chromium(III) β-diketonates conducted in hexane solution. Hexane, being a relatively poor hydrogen atom donor, has little success intercepting the photogenerated β-diketone radical (reaction 3) prior to back electron transfer from the reduced metal center (reaction 2). Consequently, no redox products survive long enough to be detected.

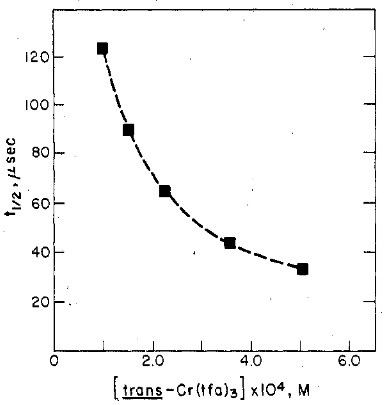


Figure 5. Effect of complex concentration on the half-time, $t_{1/2}$, characterizing the slow growth of the species X observed in flash photolysis of *trans*-$Cr(tfa)_3$ in 2-propanol.

The alternate view that the lack of redox reactivity arises from the efficient relaxation of charge-transfer excited states to lower lying ligand field states has been adopted by Zinato et al.[35] in a recent photochemical study of $Cr(acac)_3$ in ethanol–water mixtures. The basis for discounting the occurrence of redox processes in this system rested upon the failure to observe Co^{2+} when $Co(NH_3)_5F^{2+}$ is employed as a scavenger for Cr(II) species. Previous workers have noted, however, that this scavenging technique may not be a true measure of the primary redox yield.[36] Thus if back electron transfer between Cr(II) and a β-diketone radical were rapid compared to scavenging by $Co(NH_3)_5F^{2+}$, any charge-transfer activity would be obscured.[37] In view of this possibility, we feel that question of the reactivity of the charge-transfer excited states in $Cr(acac)_3$ is not entirely settled.

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Appendix

Flash photolysis of *trans*-$Cr(tfa)_3$ in alcoholic solvents causes a prompt rise in absorbance followed by a further slow growth at longer times (Figure 3). The initial process corresponds to the direct generation of the Cr(II) species, **2**, from the photoexcited complex via reactions 1–3. We attribute the latter process, on the other hand, to the additional production of **2** via an indirect route involving the reduction of ground-state *trans*-$Cr(tfa)_3$ by a species generated during the flash. This conclusion follows from the observation that the half-time, $t_{1/2}$, characterizing the slow growth in absorbance, depends upon the concentration of the complex (Figure 5).

A logical choice for the species which reduces *trans*-$Cr(tfa)_3$ is the solvent radical created via hydrogen atom abstraction

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(37) In agreement with the observation of Zinato et al.,[35] we detect negligible formation of Cr(II) upon flash photolysis of *trans*-$Cr(tfa)_3$ in a 4:1 ethanol–water mixture. This result indicates that, if back electron transfer occurs, it must be essentially complete within the ~30-μs half-life of the flash.

(reaction 3).[38] Reaction 4 describes this reduction process, while reaction 5 represents a competing pathway involving combination of two solvent radicals. According to this

$$trans\text{-Cr(tfa)}_3 + (\text{CH}_3)_2\dot{\text{C}}\text{OH} \xrightarrow{k_r} \mathbf{2} + \text{products} \quad (4)$$

$$2(\text{CH}_3)_2\dot{\text{C}}\text{OH} \xrightarrow{k_d} \text{products} \quad (5)$$

mechanism, the slow formation of the Cr(II) product can be described by the integrated rate law in eq 6, where $[\text{Cr(II)}]_{50}$

$$[\text{Cr(II)}] = [\text{Cr(II)}]_{50} + \frac{k_r[\text{Cr(III)}]}{2k_d} \times \ln\left(\frac{k_r[\text{Cr(III)}] + 4k_d[\text{Cr(II)}]_{50}}{k_r[\text{Cr(III)}] + 2k_d[\text{Cr(II)}]_{50}(1 + e^{-k_r[\text{Cr(III)}]t})}\right) \quad (6)$$

(measured 50 μs after the flash) is taken to be the initial concentration of this species, [Cr(III)] denotes the concentration of *trans*-Cr(tfa)$_3$, and *t* is time. The ratio of the Cr(II) concentrations at infinite time (>1 ms) and at 50 μs is given by eq 7. Values of $[\text{Cr(II)}]_\infty \approx 4.0 \times 10^{-6}$ M and $[\text{Cr(II)}]_{50}$

$$\frac{[\text{Cr(II)}]_\infty}{[\text{Cr(II)}]_{50}} = 1 + \frac{k_r[\text{Cr(III)}]}{2k_d[\text{Cr(II)}]_{50}} \times \ln\left(1 + \frac{2k_d[\text{Cr(II)}]_{50}}{(k_r[\text{Cr(III)}] + 2k_d[\text{Cr(II)}]_{50})}\right) \quad (7)$$

$\approx 2.0 \times 10^{-6}$ M result from flash photolysis (250 J/pulse) of a 2×10^{-4} M solution of *trans*-Cr(tfa)$_3$ in 2-propanol. Substituting these concentrations into eq 7 establishes the ratio between k_r and k_d shown in eq 8. Finally, substitution of this

$$k_r/2k_d \approx 0.4 \quad (8)$$

ratio into eq 6 leads to the rate expression given by eq 9. An

$$[\text{Cr(II)}] = [\text{Cr(II)}]_{50} + 0.4[\text{Cr(III)}] \times \ln\left(\frac{0.4[\text{Cr(III)}] + 2[\text{Cr(II)}]_{50}}{0.4[\text{Cr(III)}] + [\text{Cr(II)}]_{50}(1 + e^{-k_r[\text{Cr(III)}]t})}\right) \quad (9)$$

excellent nonlinear least-squares fit of the experimental concentrations of [Cr(II)] is obtained by using eq 9 with $k_r = (5\text{–}6) \times 10^8\ \text{M}^{-1}\ \text{s}^{-1}$.

Registry No. *trans*-Cr(tfa)$_3$, 21496-96-8.

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Photoinduced Reduction of Ru(bpy)$_3^{2+}$ by Some Dithio Anions

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The luminescing excited state Ru(bpy)$_3^{2+*}$ (bpy is 2,2′-bipyridine) is quenched in acetonitrile by a series of dithio anions like diethyldithiocarbamate (dtc$^-$). The quenching reaction involves reduction of the excited state giving Ru(bpy)$_3^+$ and the disulfide (dtc)$_2$, and its generality has been shown by using dtc$^-$ to quench a series of MLCT excited states. In the Ru(bpy)$_3^{2+*}$–dtc$^-$ system, complications in the quenching step exist because of static-quenching and specific-ion effects. It has not proven possible to build up Ru(bpy)$_3^+$ or the other reduced complexes following quenching because of slow back electron transfer between the reduced forms of the complexes and the disulfide which returns the system to its initial state. However, in multicomponent systems containing Ru(bpy)$_3^{2+}$, dtc$^-$, and a weak electron acceptor like anthraquinone or a dinitrobenzene, it is possible to build up the radical anions of the added third component which provides a powerful technique for obtaining the spectroscopic properties of the radical anions. The overall pattern of reactions also provides a conceptual basis for the design of light to chemical energy conversion schemes based on an initial excited-state reduction step.

Introduction

It has been well established that the complex Ru(bpy)$_3^{2+}$ (bpy is 2,2′-bipyridine) absorbs visible light to give a charge-transfer excited state Ru(bpy)$_3^{2+*}$ which is able to react as an electron-transfer reagent.[2] Oxidative quenching of Ru(bpy)$_3^{2+*}$ gives Ru(bpy)$_3^{3+}$ which is a strong oxidant ($E°(\text{Ru(bpy)}^{3+/2+}) = 1.3$ V vs. the saturated calomel electrode (SCE)) capable of oxidizing water to O$_2$; reductive quenching gives Ru(bpy)$_3^+$ which is a strong reductant ($E°(\text{Ru(bpy)}_3^{2+/+}) = -1.3$ V vs. SCE) capable of reducing water to H$_2$.[3] However, in most photosystems the utilization of the redox properties of photogenerated Ru(bpy)$_3^{3+}$ or Ru(bpy)$_3^+$ is prevented because of electron-transfer back-reactions which return the system to the ground state, e.g.

$$\text{Ru(bpy)}_3^{2+} \xrightarrow{h\nu} \text{Ru(bpy)}_3^{2+*}$$

$$\text{Ru(bpy)}_3^{2+*} + \text{Me}_2\text{NPh} \xrightarrow{k_q} \text{Ru(bpy)}_3^{+} + \text{Me}_2\text{NPh}^{+\cdot}$$

$$\text{Ru(bpy)}_3^{+} + \text{Me}_2\text{NPh}^{+\cdot} \xrightarrow{k_b} \text{Ru(bpy)}_3^{2+} + \text{Me}_2\text{NPh}$$

In an attempt to circumvent the back-reaction and build up Ru(bpy)$_3^+$ in solution, we have studied the utilization of some dithio anions, which are irreversible reductants, as quenchers. In particular, we have studied the series of anions I–IV, and most of our emphasis has been with the diethyldithiocarbamate anion which gave the most significant results.

Experimental Section

Materials. Spectroquality acetonitrile (MCB) was either heated at reflux for 4 h, distilled over P$_2$O$_5$, and stored over molecular sieves or used without purification from a freshly opened bottle. The photochemical properties of the systems studied did not present any differences in purified or spectroscopic solvents, except in the experiments where water was deliberately added in known concentrations in which case the dried solvent was used. Water was distilled twice from alkaline potassium permanganate.

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