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Mechanistic Photochemistry of Transition Metal β-Diketonate Complexes.
3. Detection of a New Reaction Pathway in the Ultraviolet Photochemistry of *trans*-Tris(1,1,1-trifluoro-2,4-pentanedionato)cobalt(III)

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Near-ultraviolet flash photolysis of trans-*Co(tfa)*$_3$ *(tfa is the anion of 1,1,1-trifluoro-2,4-pentanedione) in cyclohexane generates a long-lived (*$t_{1/2} \sim 3$ *sec) strongly-absorbing transient. The yield of this species decreases upon addition of good hydrogen-atom donors such as 2-propanol and tri(n-butyl)stannane. In pure 2-propanol the formation of the transient is completely suppressed, and only a bleaching of the absorbance, due to production of weakly-absorbing Co(II) products, is observed. Flashing a methanol solution of* trans-*Co(tfa)*$_3$ *produces a transient similar (but not identical) to that observed in cyclohexane; this species subsequently decays to Co(II) products. Based upon their spectral characteristics and reactivities, the flash-induced transients are assigned as Co(II) complexes containing a carbon-bonded ligand. These species result from an intramolecular rearrangement of the reduced metal-oxidized ligand radical pair formed in the primary photochemical step. Good hydrogen-atom donors can intercept this radical pair and thus inhibit transient formation. Previous mechanistic proposals about the ultraviolet photochemistry of tris(β-diketonate)cobalt(III) complexes need to be modified in view of the present results.*

Introduction

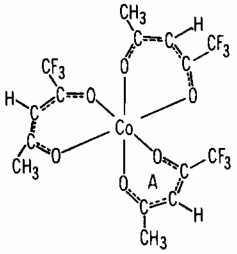
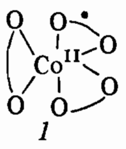


Fig. 1. Structure of *trans*-Co(tfa)$_3$; to obtain the structure of the *cis* isomer, simply permute the positions of the CH$_3$ and CF$_3$ groups in ring A.

Two previous studies have probed the photochemical reactivity of tris(β-diketonate)cobalt(III) complexes. In their investigation of Co(acac)$_3$, Co(bzac)$_3$, and Co(dbm)$_3$* in diethyl ether, Filipescu and Way [1] observed that continuous irradiation in the near-ultraviolet region induces redox behavior of the type generally associated with ligand-to-metal charge transfer. Thus the major species formed are the bis(β-diketonate)cobalt(II) complex and decomposition products of the oxidized ligand. Somewhat later, Gafney [2] reported that continuous photolysis of *cis*- or *trans*-Co(tfa)$_3$* (Fig. 1) in ethanol or hexane produces Co(tfa)$_2$ and the protonated ligand, H(tfa). While the quantum efficiency of the photoredox pathway exhibits no dependence upon isomeric identity, it drops by a factor of three upon changing from the alcohol to the hydrocarbon solvent.

The mechanism shown below (the specific example of *trans*-Co(tfa)$_3$ is considered) has been proposed to account for these results [1–3]. Photoexcitation of the parent complex (reaction 1) to a ligand-to-metal charge transfer state generates

$$trans\text{-Co}^{III}(\text{tfa})_3 \underset{}{\overset{h\nu}{\rightleftharpoons}} trans\text{-Co}(\text{tfa})_3^{*} \qquad (1)$$

trans-Co(tfa)$_3$* →  (2)

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*Ligand abbreviations: acac (2,4-pentanedionato); bzac (1-phenyl-1,3-butanedionato); dbm (1,3-diphenyl-1,3-propanedionato); tfa (1,1,1-trifluoro-2,4-pentanedionato).

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$$1 \longrightarrow trans\text{-Co(tfa)}_3 \qquad (3)$$

$$1 \longrightarrow \text{Co(tfa)}_2 + \text{tfa}^{\bullet} \qquad (4)$$

$$1 \xrightarrow{\text{SH}} \text{Co(tfa)}_2 + \text{H(tfa)} + \text{S}^{\bullet} \qquad (5)$$

a species, *1*, that formally contains Co(II) bound to a β-diketone radical (reaction 2). In ensuing steps, *1* may undergo (i) back-electron transfer to regenerate the original complex (reaction 3), (ii) expulsion of the ligand radical (reaction 4) which then reacts rapidly via intramolecular (*e.g.* fragmentation) and/or intermolecular (*e.g.* O_2 scavenging) pathways, or (iii) abstraction of a hydrogen atom from the solvent, SH, with the concomitant formation of free H(tfa) (reaction 5).

Incidental to another photochemical study in our laboratory, we had occasion to flash photolyze cyclohexane solutions of *trans*-Co(tfa)$_3$. It became apparent from initial results that the reactivity of the complex on the short time scale of the flash experiment is not adequately described by the mechanistic sequence presented above. In particular, we observe a transient species whose properties support its formulation as a Co(III) complex containing a carbon-bonded ligand. Moreover, the formation of this transient and its subsequent decay are strongly affected by the addition of 2-propanol to the system. These unexpected findings prompted us to undertake a detailed study of the flash-induced behavior of *trans*-Co(tfa)$_3$ in several nonaqueous solvents. A complete account of our results is reported here.

Experimental

Reagents

Commercially available Co(tfa)$_3$ (Research Organic/Inorganic Chemical Corp.) was purified by dissolving a sample in benzene, washing the solution three times with 10% NaOH, and drying the benzene layer with $MgSO_4$. Separation into *cis* and *trans* isomers was accomplished by chromatography on a 100 cm × 2.5 cm glass column packed with 60–200 mesh silica gel, using a 75% hexane–25% benzene solvent mixture as the eluant. The separation procedure was conducted in the dark to avoid photodecomposition. The melting point of the *trans* isomer (156–157 °C) agreed closely with the literature value [4] (158–158.5 °C), and the isomeric purity was confirmed by gas chromatography [5].

The monohydrate of Co(tfa)$_2$ was prepared by a procedure [6] similar to that reported for Co(acac)$_2$. An analytically pure sample was obtained after twice subliming the crude product at 80–90 °C under vacuum. *Anal.* Calc. for Co(tfa)$_2$·H_2O: C, 31.33; H, 2.61. Found: C, 31.33; H, 2.63.

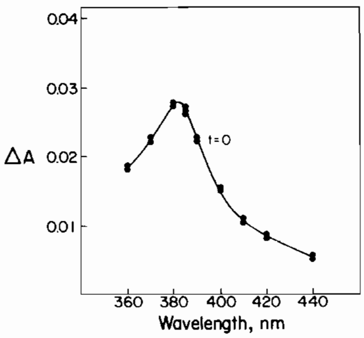


Fig. 2. Spectrum of the transient, X, generated in the flash photolysis of *trans*-Co(tfa)$_3$ in cyclohexane. The absorbance readings are extrapolated back to zero time.

Flash Photolysis Procedures

Since the flash apparatus employed in the present study has been described previously [7], only a few of the more important characteristics will be noted here. Pulses of polychromatic light ($\lambda \geqslant 240$ nm) having a half-life of ~30 μsec were obtained from two xenon flash lamps fired in series at stored electrical energies $\leqslant$250 J/pulse. Cut-off filters were used to isolate different spectral regions. Photogenerated transients were detected optically with an analyzing light beam directed through the sample cell. The output of the detector phototube was filtered from high-frequency noise and off-set by a sample-and-hold circuit. Transient responses were converted from analog to digital in a 805 Waveform Recorder (Biomation) and processed in a PDP-8L computer (Digital).

Sample solutions were prepared by dissolving *trans*-Co(tfa)$_3$ in solvents which had been deaerated by bubbling with solvent-saturated argon. Following each flash irradiation, the photolyte in the cell was replaced with fresh solution. All solvents were spectral grade quality: cyclohexane was dried over molecular sieves, while methanol and 2-propanol were used as received.

Results

Flash photolysis of *trans*-Co(tfa)$_3$ in deaerated cyclohexane reveals a transient, X, with a differential absorption maximum at ~380 nm (Fig. 2). The transient is formed during the flash, and thereafter undergoes a slow first-order decay with a half-life of ~3 sec. The initial absorbance change at 380 nm, extrapolated back to zero time, provides a convenient measure of the amount of X generated by the flash. This initial yield varies linearly with the flash intensity and becomes negligible for excitation at wavelengths > 360 nm.

Addition of 2-propanol to cyclohexane solutions of *trans*-Co(tfa)$_3$ modifies the behavior of X. Thus

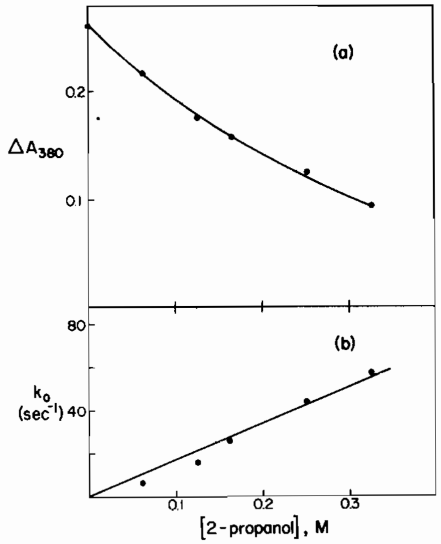


Fig. 3. Dependence of (a) initial yield and (b) rate of the 380 nm absorbance decay of transient X on alcohol concentration in 2-propanol/cyclohexane solvents. The flash energy was 250 J.

the amount of this species produced decreases with the increasing 2-propanol concentration (Fig. 3a). The rate at which X decays, on the other hand, is enhanced by the presence of the alcohol (Fig. 3b); the pseudo first-order rate constant describing this dependence is given by the expression

$$k_{obs} = (0.21 \pm 0.02) + (1.5 \pm 0.2) \times 10^2 [\text{2-propanol}]$$

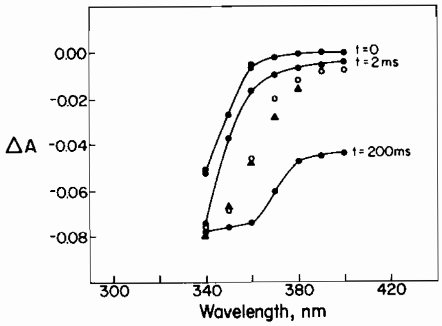


Fig. 4. Spectra observed (●) at various times following flash photolysis of *trans*-Co(tfa)$_3$ in 2-propanol (⩾95%)/cyclohexane solutions. Spectrum calculated (▲) on assumption that *trans*-Co(tfa)$_3$ and Co(tfa)$_n^{+(2-n)}$ (n ⩽ 2) are the only absorbing species in the photolyte. Absorbance change (○) observed upon continuous photolysis of *trans*-Co(tfa)$_3$ at 313 nm. Relative values of ΔA are used for the latter two spectra.

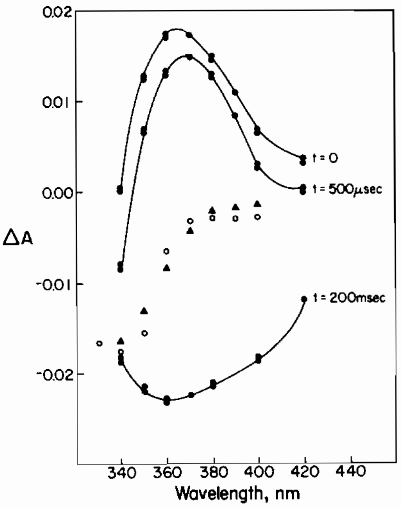


Fig. 5. Spectra observed (●) at various times following flash photolysis of *trans*-Co(tfa)$_3$ in methanol; t = 0 spectrum corresponds to transient X′. Spectrum calculated (▲) on assumption that *trans*-Co(tfa)$_3$ and Co(tfa)$_n^{+(2-n)}$ (n ⩽ 2) are the only absorbing species in the photolyte. Absorbance change (○) observed upon continuous photolysis of *trans*-Co(tfa)$_3$ at 313 nm. Relative values of ΔA are used for the latter two spectra.

At high (>95%) 2-propanol concentrations, no transient absorption due to X is observed. Instead, a prompt bleaching of the spectrum occurs in the 340–380 nm region (Fig. 4). This bleaching continues to increase with time in three discernible stages. The fastest stage (monitored at 340 nm) follows the prompt bleaching of the absorbance and is characterized by a first-order rate constant of $(2.2 \pm 0.2) \times 10^3$ sec^{-1}. Thereafter, a further bleaching at wavelengths ⩾340 nm occurs by a first order process with a rate constant of $(1.7 \pm 0.3) \times 10^1$ sec^{-1}. Additional spectral changes, detected at times >1 sec following the flash, can be described as an increase in the absorbance at 360 nm and a bleaching at 340 nm. Two lines of evidence indicate that the bleaching observed upon flash photoysis of *trans*-Co(tfa)$_3$ in 2-propanol results from the formation of Co(II) photoproducts. First, comparison of the experimental spectra with one calculated on the assumption that the only absorbing species in the 340–400 nm region are unreacted *trans*-Co(tfa)$_3$ and solvated [8] Co(tfa)$_n^{+(2-n)}$ (n ⩽ 2) products reveals a definite similarity (Fig. 4). Since the photolyzed solution may contain absorbing products derived from the oxidized ligand, we also measured the spectral change (difference in absorbance of photolyzed *vs.* dark sample) that results from continuous irradiation of *trans*-Co(tfa)$_3$ in 2-propanol. This differential spectrum (Fig. 4), which reflects the formation of Co(II) products [2], also bears a close resemblance to the spectra observed in flash photolysis.

A few flash experiments were performed on cyclohexane solutions of *trans*-Co(tfa)$_3$ containing tri(n-butyl)stannane, HSn(n-Bu)$_3$. Even modest concentrations (⩾0.1 *M*) of this potent hydrogen atom donor [9] effectively inhibit the formation of X. As is the case with concentrated 2-propanol solutions, only a bleaching of the absorbance at wavelengths <380 nm occurs.

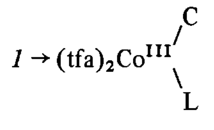
The behavior observed upon flash irradiation of *trans*-Co(tfa)$_3$ in deaerated methanol is especially interesting in that it combines the major features seen in other solvent systems. Thus the flash generates a prompt transient, X$'$, with an absorption spectrum (Fig. 5) similar to, but somewhat blue-shifted from that of X in pure cyclohexane. Decay of this transient occurs via a first-order process with a rate constant of $(1.0 \pm 0.2) \times 10^3$ sec^{-1}. The decay is followed by a slow bleaching of the absorbance analogous to the one observed in concentrated 2-propanol solutions. This process obeys first-order kinetics with a rate constant of $(7.7 \pm 0.4) \times 10^1$ sec^{-1}. Further spectral changes, detected at times >1 sec after the flash, result in a shift of the ~360-nm minimum to shorter wavelengths. The spectral characteristics observed at these long times are again indicative (Fig. 5) of the formation of Co(II) photoproducts.

Discussion

Reactions 1–5 summarize the behavior expected [1–3] upon near-ultraviolet irradiation of *trans*-Co(tfa)$_3$. Thus the primary photochemical act is generally regarded to be the formation of a reduced metal-oxidized ligand radical pair, *1*. In subsequent steps this species partitions between pathways that either regenerate the parent complex or lead *directly* to the final redox products. Because the short lifetime of *1* [10] would preclude its detection by the flash apparatus employed in the present study, the only observable consequence of flash photolyzing *trans*-Co(tfa)$_3$ is predicted to be a prompt bleaching of the absorbance in the 330–400 nm region corresponding to the production of Co(tfa)$_2$ or other weakly-absorbing Co(II) products. While such behavior does obtain in some solvents, the detection of a long-lived, strongly-absorbing transient in cyclohexane (X) and methanol (X$'$) indicates that a previously unsuspected reaction channel must be available to *1*.

Some insight as to the identities of X and X$'$ and their mode of formation can be obtained by consideration of the reported photochemical properties of formato- and oxalatoammine complexes of Co(III) in aqueous solution [11, 12]. The 254-nm photolysis of $Co(NH_3)_4C_2O_4^+$, for example, results in the parallel production of $Co^{+2}_{(aq)}$ and a metastable C-bonded formato complex of Co(III), $(NH_3)_4(OH_2)CoCoH_2H^{+2}$. Formation of the latter species involves heterolytic C–C bond scission within the oxalate ligand, loss of CO$_2$, and Co–O to Co–C linkage isomerization. This metastable Co(III) complex, which displays an absorption maximum at ~265 nm, decays via internal electron transfer to produce additional $Co^{+2}_{(aq)}$ and the formyl radical.

We propose that the transients, X and X$'$, observed in the flash photolysis of *trans*-Co(tfa)$_3$ result from an intramolecular rearrangement of the photogenerated radical pair, *1* (reaction 6) [13]. The intramolecular nature of this process accounts for the observed linear dependence of the initial yield of X upon light intensity (*vide supra*). Both X and X$'$ are assigned as Co(III) complexes containing a carbon-bonded ligand. We favor this description on grounds that the spectral characteristics of both



$$1 \rightarrow (tfa)_2Co^{III}\begin{matrix}/\,C\\ \backslash\,L\end{matrix} \qquad (6)$$

X (in C_6H_{12})
X$'$ (in CH_3OH)

species (Figs. 2 and 5) are consistent with Co(III) rather than Co(II) complexes [11, 12]. Moreover, the conversion of the transients to Co(II) products (Fig. 5) parallels the behavior of the C-bonded formato complex generated in the photolysis of $Co(NH_3)_4C_2O_4^+$. The precise stoichiometries of X and X$'$ are not established by the present results. In the generalized structure given for the complexes (reaction 6), C represents the carbon-bonded ligand and L denotes a sixth group needed to complete the coordination sphere of the metal. Possibilities for C include a carbon-bonded tfa$^-$ or some fragment derived from the precursor ligand radical; L could be a solvent molecule or perhaps another ligand fragment. Because the identities of L and C can vary with changes in solvent, it is not surprising that X and X$'$ possess different absorption spectra.

Formation of X or X$'$ (reaction 6) competes with those pathways (reactions 4 and 5) that lead directly to Co(II) products*. In a good hydrogen atom donor solvent such as 2-propanol, reaction 5 will assume enhanced importance relative to reaction 6. This competition accounts for the decrease in the initial yield of X as the alcohol content in 2-propanol/cyclohexane solvents is increased (Fig. 3a). At sufficiently high concentrations of 2-propanol, the formation of X is completely suppressed and only a prompt

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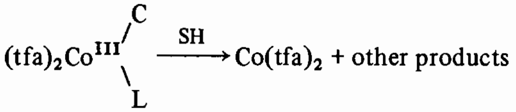
*While our results do not rule out the possibility that X or X$'$ originates from an excited state different from that responsible for direct Co(II) production [11, 12], neither do they require it. Thus we prefer the simpler mechanism involving a single photoactive charge-transfer-to-metal excited state and its radical-pair successor, *1*.

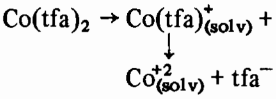
bleaching of the spectrum of *trans*-Co(tfa)$_3$ is observed (Fig. 4). A similar explanation applies to the inhibitory effect of HSn(n-Bu)$_3$. The redox process that converts X and X′ to Co(II) products (reaction 7) also depends upon solvent composition as evidenced by the considerably more rapid disappearance of the transient absorbance in alcohols than in cyclohexane.



$$(\mathrm{tfa})_2\mathrm{Co}^{\mathrm{III}}\!\begin{array}{l}/\mathrm{C}\\ \backslash\mathrm{L}\end{array} \xrightarrow{\mathrm{SH}} \mathrm{Co(tfa)_2} + \text{other products} \qquad (7)$$

Such behavior may simply reflect the sensitivity of the electron-transfer rate constant to changes in solvent properties (*e.g.* polarity, solvating ability); however, a direct reaction of the transient with a reducing alcohol molecule cannot be ruled out.

The nature of the process responsible for the fast stage (rate constant of 2.2 X 10^3 sec^{-1}) of the absorbance bleaching observed in 2-propanol cannot be ascertained from the present results. Two possibilities are secondary reduction of *trans*-Co(tfa)$_3$ by the solvent radical produced in reaction 5 [14], and structural relaxation of the Co(tfa)$_2$ species initially formed from *1*. The slow bleaching of the absorbance in methanol and 2-propanol solutions at long times (>1 msec) following the flash is most likely associated with the solvolysis of Co(tfa)$_2$ (reaction 8). Thus Meisel *et al.* [14] report that the analogous compound,



$$\begin{array}{l}\mathrm{Co(tfa)_2} \rightarrow \mathrm{Co(tfa)^+_{(solv)}} + \mathrm{tfa^-} \\ \qquad\qquad\quad \downarrow \\ \qquad\qquad\ \mathrm{Co^{+2}_{(solv)}} + \mathrm{tfa^-}\end{array} \qquad (8)$$

Co(acac)$_2$, undergoes stepwise dissociation of its ligands in aqueous solution with rate constants of 30 and 3 sec^{-1}.

Finally, it is interesting to compare the ultraviolet photochemistries of *trans*-Co(tfa)$_3$ and the analogous Cr(III) [5] and Rh(III) [15] complexes. In each case the population of an excited state containing appreciable ligand-to-metal charge transfer character results in the formation of a reduced metal-oxidized ligand radical pair. This reactive species can undergo a variety of secondary processes, including back-electron transfer with concomitant geometrical isomerization (Cr, Rh), intramolecular rearrangement to a trivalent complex containing a carbon-bonded ligand (Co), and formation of solvated M(tfa)$_2$ (Co, Cr, Rh). The relative importance of these pathways depends upon the metal and thus reflects the different reactivities of the divalent oxidation states.

Conclusions

Flash photolysis reveals that a long-lived transient can mediate in the redox decomposition of *trans*-Co(tfa)$_3$ in nonaqueous solvents. Based upon its spectral characteristics and decay to Co(III) products, the transient is assigned as a Co(II) complex containing a carbon-bonded ligand. The mechanism (reactions 1–5) previously proposed to explain the ultraviolet photochemistry of tris(β-diketonate)-cobalt(III) complexes should now be expanded to include the formation (reaction 6) and reactivity (reaction 7) of this interesting species.

Acknowledgements

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