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Steric Effects in Photoisomerization of Chromium (III) β-Diketonate Complexes[1]

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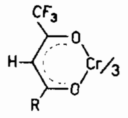
Photoisomerization and photoresolution are well-established phenomena for tris(β-diketonato)chromium(III) complexes [2–8]. Recently we carried out a detailed study of photoisomerization of the Cr(III) complex of a chiral β-diketone, (+)-3-acetylcamphor, hereafter abbreviated $Cr(atc)_3$, in an effort to determine the mechanism by which photoisomerization occurs [8]. Photoisomerization occurs among all four diastereomers of $Cr(atc)_3$ upon irradiation at several wavelengths in the visible and ultraviolet regions. An analysis of quantum yield ratios strongly suggests the mechanism involves bond rupture, forming a square pyramidal transition state or intermediate with the dangling ligand axial.

Isomerization quantum yields for irradiation of the d–d band of $Cr(atc)_3$ are of the same order of magnitude as those found by Stevenson and Driesche [5] for photolysis of the d–d band of tris(1,1,1-trifluoro-2,4-pentanedionato)chromium(III), I(R = CH_3), abbreviated $Cr(mfa)_3$.



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However in an earlier study of tris(1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionato)chromium(III), I(R= t-butyl), abbreviated $Cr(bfa)_3$, no isomerization was found upon irradiation of the d–d band [3]. Since $Cr(bfa)_3$ differs from $Cr(mfa)_3$ only in replacement of the methyl substituent by a t-butyl group, the absence of photoisomerization in the former complex was deemed to be a steric effect with possible interesting mechanistic implications. We decided to examine the effect of a substituent of intermediate steric requirement on the photoisomerization of complexes I. Thus *cis* and *trans* isomers of tris(1,1,1-trifluoro-5-methylhexane-2,4-dionato)chromium(III), I(R = i-propyl), abbreviated $Cr(pfa)_3$ were photolyzed in the region of the d–d transition. Photoisomerization does indeed occur, but an unexpectedly large difference in quantum yields for *cis→trans* and *trans→cis* isomerization has been found. Similar results were subsequently found for $Cr(bfa)_3$.

Experimental

$Cr(pfa)_3$ and $Cr(bfa)_3$ were prepared by the method used previously to prepare $Cr(atc)_3$ [9] and were separated into *cis* and *trans* isomers by preparative layer chromatography on 20 X 20 cm silica gel plates (2 mm layer) using a 9:1 (v/v) heptane: THF solvent mixture. $Co(pfa)_3$ was prepared by the method reported [10] for $Co(mfa)_3$ and was chromatographed under the above conditions. The faster moving chromatographic band for $Co(pfa)_3$ proved to contain the *trans* isomer as deduced from comparison of the proton nmr spectra of the two products [11]. Isomers for all three complexes were extracted from the silica gel using methanol. After evaporation of the methanol, the isomers were purified by extraction with CCl_4 followed by evaporation of the solvent to yield crystalline products which gave the following analyses on an F and M Model 185 C, H, and N analyzer: $Cr(pfa)_3$: Calcd: C, 42.36; H, 4.06. Found: (*cis*) C, 42.35; H, 4.03; (*trans*) C, 42.61; H, 4.09. $Cr(bfa)_3$: Calcd: C, 45.22; H, 4.74. Found: (*cis*) C, 45.86; H, 4.97; (*trans*) C, 45.90; H, 4.83. $Co(pfa)_3$: Calcd: C, 41.88; H, 4.02. Found: (*cis*) C, 42.50; H, 4.33; (*trans*) C. 42.31; H, 4.21.

Photolysis was carried out using a Sargent-Welch 200 watt super pressure mercury lamp filtered by $CuCl_2$ and $K_2Cr_2O_7$ solutions which transmit light of ~40 nm bandwidth centered about 577 nm [12]. Solutions (6.73×10^{-3} *M*) of *cis* or *trans* isomers in spectral grade n-hexane were photolyzed in a cylindircal cell of 2 cm path length. Under these conditions 88% of the incident light is absorbed. Aliquots (0.2 ml) were removed at two-hour intervals. The light absorbed per unit time for the cell used (I'_a), determined using aqueous Reinecke's salt [13], was 1.72×10^{-7} E/sec.

The composition of each aliquot was determined quantitatively by high pressure liquid chromatography using conditions described previously [8] except that a solvent mixture of 0.5% THF in n-hexane was used as the eluant with a flow rate of 0.18 ml/min. Initial quantum yields for formation of *trans* isomers from photolysis of *cis* isomers and *vice versa* were determined from the chromatographic signal areas as described in detail previously [8].

Results and Discussion

$Co(pfa)_3$ was prepared in order to assist in identifying the *cis* and *trans* isomers of $Cr(pfa)_3$. The Co(III) complex is diamagnetic, thus nmr may be used to distinguish *cis* and *trans* isomers. $Co(pfa)_3$ and $Cr(pfa)_3$ differ only in the metal ion, and corresponding isomers should have very similar chromatographic behavior under the same conditions [9, 14–15]. Thus the more intense, faster moving plc band for $Cr(pfa)_3$ is believed to contain the *trans* isomer (see Experimental).

Irradiation of the visible absorption band (λ_{max} = 567 nm, ϵ_m = 77) of *cis*-$Cr(pfa)_3$ results in formation of the *trans* isomer with a quantum yield, $\phi_{c\rightarrow t}$, of 0.93 (±0.10) X 10^{-3}. No other photolysis products were detected. Since *cis*-$Cr(pfa)_3$ exists in enantiomeric forms (Δ and Λ), this quantum yield represents combined quantum yields for the processes Λ-*cis*→Λ-*trans* and Λ-*cis*→Δ-*trans* (which have identical quantum yields as the processes Δ-*cis*→Δ-*trans* and Δ-*cis*→Λ-*trans*, respectively). On the other hand, extensive photolysis of *trans*-$Cr(pfa)_3$ yielded barely detectable amounts of the *cis* isomer. After photolysis for 24 hr a measurable chromatographic signal for the *cis* isomer was obtained, and a quantum yield $\phi_{t\rightarrow c} \leqslant 0.05$ (±0.02) X 10^{-3} was calculated. $\phi_{t\rightarrow c}$ represents combined quantum yields for the processes Λ-*trans*(Δ-*trans*)→Λ-*cis*(Δ-*cis*) and Λ-*trans* (Δ-*trans*)→Δ-*cis*(Λ-*cis*). These quantum yields are compared in Table I with the corresponding quantum yields obtained by Stevenson and Driesche [5] for the closely related complex $Cr(mfa)_3$.

TABLE I. Quantum Yields for Photoisomerization.

	$10^3\phi_{c\rightarrow t}$	$10^3\phi_{t\rightarrow c}$	Ratio $\phi_{t\rightarrow c}/\phi_{c\rightarrow t}$
$Cr(pfa)_3$[a]	0.93 ± 0.10	≤0.05 ± 0.02	≤0.05
$Cr(mfa)_3$[b]	4.8 ± 1.2[c]	0.95 ± 0.24[c]	0.20

[a] In n-hexane solution; 577 nm. [b] In chlorobenzene solution; 546 nm (data from ref. 5). [c] These numbers are sums of quantum yields reported for the individual pathways [5].

Differences in the *overall* quantum yields found for $Cr(mfa)_3$ and $Cr(pfa)_3$ are within the range of differences found for β-diketonate complexes of Cr(III) and attributed to substituent effects [7]. Also the influence of the different solvents (n-heptane *vs.* chlorobenzene) on overall quantum yields is unknown. Of primary interest here is the striking difference in *ratios* of quantum yields $\phi_{t\rightarrow c}/\phi_{c\rightarrow t}$ for $Cr(mfa)_3$ and $Cr(pfa)_3$ (Table I), although the d–d band was irradiated in each case. Earlier work indicated that photolysis of Cr(III) β-diketonate complexes results in Cr–O bond rupture [8], and formation of products from the five-coordinate intermediate is believed to be thermally controlled. Statistically, $\phi_{t\rightarrow c}/\phi_{c\rightarrow t}$ is 0.33, assuming equal utilization of absorbed light by each isomer in forming the five-coordinate complex. The quantum yield ratios given in Table I are less than statistical in each case, and deviation from the statistical ratio is greater for the complex having the bulkier substituent. A possible explanation is that *cis* isomers are more efficient in use of photochemical energy for bond breaking as a result of greater steric strain (*i.e.*, non-radiative decay is greater for *trans* isomers). The larger steric strain expected for *cis*-$Cr(pfa)_3$ compared to *cis*-$Cr(mfa)_3$ would account for the smaller $\phi_{t\rightarrow c}/\phi_{c\rightarrow t}$ ratio for $Cr(pfa)_3$. An alternative explanation assumes both isomers utilize light with approximately equal efficiency for bond breaking, but steric effects during the thermal formation of products from the five-coordinate intermediate favor *trans* isomers.

These arguments predict a small $\phi_{t\rightarrow c}/\phi_{c\rightarrow t}$ ratio also for $Cr(bfa)_3$ where R = t-butyl, but $\phi_{c\rightarrow t}$ should be measurably large in contrast to the earlier report by Koob *et al.* [3]. To test this hypothesis, the isomers of $Cr(bfa)_3$ (λ_{max} = 566 nm) were photolyzed under the same conditions used for $Cr(pfa)_3$. Results of tlc analysis of the photoreaction products of *cis*- and *trans*-$Cr(bfa)_3$ were qualitatively very similar to tlc results obtained for $Cr(pfa)_3$ isomers. We conclude that Koob *et al.* did not irradiate $Cr(bfa)_3$ with a sufficient number of photons to detect isomerization.

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