

Evidence for a Second Photoactive Excited State in a Tris(β -diketonate)chromium(III) Complex

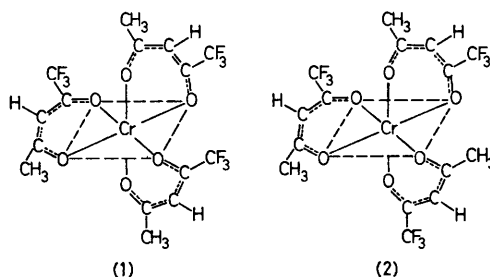
By DARCHUN B. YANG and CHARLES KUTAL*

(Department of Chemistry, University of Georgia, Athens, Georgia 30602)

Summary Photolysis of *trans*-tris(1,1,1-trifluoropentane-2,4-dionato)chromium(III) in nonaqueous solvents induces both geometrical isomerization and decomposition, with the quantum efficiency of the latter pathway exhibiting an appreciable solvent dependence.

PREVIOUS photochemical studies¹ of tris(β -diketonate)-chromium(III) complexes have established the generality of stereochemical rearrangement as an excited-state pathway. We now report the observation of a second photoinduced process, decomposition of the complex, upon irradiation of *trans*-Cr(tfpd)₃ (tfpdH = 1,1,1-trifluoropentane-2,4-dione) in nonaqueous solvents.

Cr(tfpd)₃ was prepared and separated into *trans*-(1) and *cis*-(2) isomers by a published procedure.² Irradiation at 254 nm was accomplished with a low-pressure mercury lamp (> 92% output at this wavelength) while a high-pressure mercury lamp with appropriate interference and blocking filters was employed at longer wavelengths. Light intensity was measured by ferrioxalate³ or reineckate⁴



actinometry. *trans*-*cis* isomerization and decomposition of *trans*-Cr(tfpd)₃ were monitored by gas chromatography under conditions similar to those employed in an earlier study.²

We have found the photochemical behaviour of *trans*-Cr(tfpd)₃ to be considerably more diverse than that previously reported for tris(β -diketonate)chromium(III) complexes.¹ The key observations (Table) may be summarized

TABLE. Photochemical behaviour of *trans*-Cr(tfpd)₃ (1).

Wavelength irradiated nm	Benzene		Cyclohexane		Propan-2-ol	
	$\phi_{\text{isom.}}$	$\phi_{\text{dec.}}$	$\phi_{\text{isom.}}$	$\phi_{\text{dec.}}$	$\phi_{\text{isom.}}$	$\phi_{\text{dec.}}$
546	$6.7 \pm 0.6 \times 10^{-4}$	$< 1 \times 10^{-4}$	— ^a	—	—	—
408	$8.1 \pm 1.1 \times 10^{-4}$	$< 2 \times 10^{-5}$	—	—	$1.4 \pm 0.04 \times 10^{-3}$	—
366	$9.0 \pm 0.2 \times 10^{-4}$	$< 2 \times 10^{-4}$	$8.8 \pm 0.7 \times 10^{-4}$	$< 6 \times 10^{-6}$	$1.5 \pm 0.1 \times 10^{-3}$	$2.8 \pm 0.5 \times 10^{-4}$
254 ^b	—	—	$3.2 \pm 0.1 \times 10^{-3}$	$2.2 \pm 0.1 \times 10^{-3}$	$2.4 \pm 0.1 \times 10^{-3}$	$2.4 \pm 0.1 \times 10^{-2}$
			$2.3 \pm 0.1 \times 10^{-3}$ ^c	$6.6 \pm 0.4 \times 10^{-3}$ ^c		

^a A dash indicates that no data were recorded under the stated conditions. ^b Solutions irradiated at 254 nm were degassed by 3 freeze-thaw cycles. ^c Solution contains a 13-fold excess of the ready hydrogen atom donor, HSnBu₃ (see W. Trotter and A. C. Testa, *J. Amer. Chem. Soc.*, 1968, **90**, 7044).

as follows. (i) *trans* to *cis* isomerization with essentially wavelength-independent quantum yield is the sole detectable process in benzene or cyclohexane solution upon irradiation at wavelengths > 366 nm. (ii) In contrast, both isomerization and decomposition ($\phi_{\text{dec.}}/\phi_{\text{isom.}} = 0.19$) occur at 366 nm in propan-2-ol. (iii) The latter pathway assumes major importance ($\phi_{\text{dec.}}/\phi_{\text{isom.}} = 0.69$ in cyclohexane and 10 in propan-2-ol) at 254 nm; furthermore, free tfpdH can be detected in the photolyte. (iv) A qualitative correlation exists between $\phi_{\text{dec.}}$ and the hydrogen atom donor ability of the solvent or other species (*e.g.* HSnBu₃) present in solution.

Several mechanistic insights emerge from consideration of the above behaviour. The observation of two photoinduced processes with a wavelength-dependent quantum yield ratio ($\phi_{\text{dec.}}/\phi_{\text{isom.}}$) provides the first compelling evidence for the participation of at least two photoactive excited states in a tris(β -diketonate)chromium(III) complex. We associate the strong preference for isomerization at longer wavelengths with the population of the lowest quartet ligand field excited state (4A_1 or 4E if the effective symmetry is D_3). The stereomobility of this state in Cr^{III} complexes is well documented;⁵ furthermore, the constancy of $\phi_{\text{isom.}}$ implies that the quartet is efficiently populated

via relaxation from higher excited states lying in the 366–546 nm wavelength region.

The sharp increase in $\phi_{\text{dec.}}$ at wavelengths ≤ 366 nm indicates the presence of a second photoactive state in *trans*-Cr(tfpd)₃ which favours decomposition. While the identity of this state is not definitively established by our results, the observed photoreactivity suggests that it possesses considerable ligand-to-metal charge transfer character.⁶ This type of photoinduced electron transfer formally generates Cr^{II} bound to a β -diketone radical. In subsequent steps this distorted⁷ and undoubtedly highly reactive species could partition between two competing paths: (A) back electron transfer with regeneration of the original complex or its corresponding isomer, or (B) hydrogen atom abstraction from the solvent (or HSnBu₃) with resulting decomposition of the trischelate complex. Such behaviour accommodates both the observed increase in $\phi_{\text{isom.}}$ upon irradiation at 254 nm (path A) and the appreciable solvent dependence of $\phi_{\text{dec.}}$ (path B).

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