Detection of a Photoredox Pathway in a Tris(β-diketonate)chromium(III) Complex

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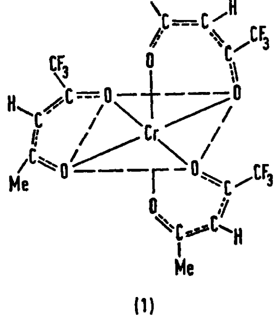
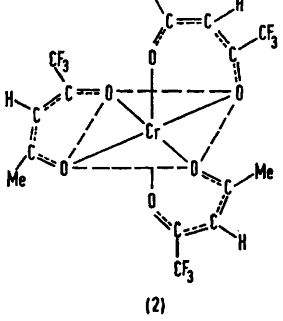
Summary Flash photolysis of *trans*-tris(1,1,1-trifluoropentane-2,4-dionato)chromium(III) in propan-2-ol–cyclohexane yields a Cr^{II}-containing product *via* a solvent-dependent photo-redox pathway.

ULTRAVIOLET irradiation of the β-diketonate complexes of most first row transition metals (*e.g.* Mn, Fe, Co, Ni, and Cu) results in a one-electron reduction of the metal centre by the ligand.[1a] The notable exception to this general pattern has been chromium, whose complexes favour stereochemical rearrangement to the apparent exclusion of photoredox processes.[2–5] Recently, however, we reported that photolysis of *trans*-$Cr(tfpd)_3$ (tfpdH = 1,1,1-trifluoropentane-2,4-dione) in a variety of nonaqueous solvents induces both *trans* (**1**) to *cis* (**2**) isomerization and decomposition of the complex with the release of free tfpdH.[6]


(1)


(2)

While isomerization is an expected consequence of populating the lowest quartet ligand field excited state in Cr^{III},[1b] the dependence of the quantum yield of decomposition (ϕ_{dec}) on the hydrogen atom donor ability of the solvent led us to suggest that this pathway originates from an excited state containing appreciable ligand-to-metal charge transfer character. We now present the results of a flash photolysis study which corroborate this latter assignment.

Sample solutions were prepared by dissolving the pure *trans* complex[7] in solvents which had been deaerated by bubbling with argon. Flash irradiations were performed using an apparatus described previously.[8] Pulses of polychromatic light ($\lambda \geqslant 240$ nm) ($t_{\frac{1}{2}}$ *ca.* 30 μs) were obtained for stored electrical energies of 60—250 J/pulse. Blocking filters placed in the path of the exciting light were used to isolate various wavelength regions.

We find that flash photolysis of *trans*-$Cr(tfpd)_3$ in propan-2-ol–cyclohexane generates a metastable species, X, which displays a differential absorption maximum at *ca.* 350 nm. The yield of X produced by the flash (as measured by the change in absorbance, ΔA, at 350 nm) increases as the alcohol content of the solvent is increased (Table).

TABLE Yield (ΔA) of the metastable intermediate, X, generated in the flash photolysis of *trans*-$Cr(tfpd)_3$

ΔA	Conditions[a]
0.010	100% Cyclohexane; 250 J/pulse
0·072	40% Propan-2-ol in cyclohexane; 250 J/pulse
0·190	100% Propan-2-ol; 250 J/pulse
0·092	100% Propan-2-ol; 120 J/pulse
0·053	100% Propan-2-ol; 62 J/pulse

[a] Deaerated solutions; $[Cr(tfpd)_3] = 7{\cdot}5 \times 10^{-5}$ M

Detectable amounts of X are formed only upon excitation with light of wavelength ⩽330 nm. These results closely parallel the solvent and wavelength responses of ϕ_{dec} measured under continuous photolysis conditions,[6] thereby suggesting that X originates from the excited state which is also responsible for decomposition of the complex. The half-life for the disappearance of X in deaerated propan-2-ol is considerably longer than the limit of measurement of our apparatus ($t_{\frac{1}{2}} > 10$ s). Introduction of air or other oxidants such as Cu^{2+} or Fe^{3+} ions into the solution, however, causes a marked reduction of the half-life ($t_{\frac{1}{2}}$ *ca.* 0·8 s in air-saturated solution). This behaviour clearly established X as a reducing species.

An explanation for these and previous[6] observations is that *trans*-$Cr(tfpd)_3$ possesses a photoactive excited state with considerable ligand-to-metal charge transfer character. The immediate consequence of populating this state is the production of a reactive Cr^{II}-ligand radical species whose subsequent fate depends upon the solvent. In cyclohexane, back electron transfer with regeneration of the original complex (or its *cis* isomer) is favoured, whereas a better hydrogen atom donor such as propan-2-ol can scavenge the tfpd ligand radical (forming tfpdH) prior to recombination. Such scavenging leads to an accumulation of the metastable product, X, which we identify as a Cr^{II}-containing species[9] [probably solvated $Cr(tfpd)_2$].

This relatively efficient photoredox pathway in *trans*-$Cr(tfpd)_3$ provides the first indication that the u.v. photochemistry of Cr^{III} β-diketonates is qualitatively similar to that of other first row transition metal β-diketonate complexes. We conclude that the failure to observe this pathway in earlier studies[2,4,5] of Cr^{III} resulted from the use of poor hydrogen atom donor solvents (*e.g.* hexane or aqueous mixtures) which are unable to intercept efficiently the photogenerated ligand radical prior to its recombination with the reduced metal centre.

We thank the Office of Basic Energy Sciences, Department of Energy for partial support.

(*Received, 27th June* 1979; *Com.* 677.)

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