The Direct and Sensitized Photoisomerization of 1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dionatochromium(III)

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Summary cis- and *trans*-1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dionatochromium(III) have been photolysed and found to reach a photostationary state in which the two isomers are in the same ratio as at thermally-induced equilibrium; quenching of the photoreaction of triplet methyl *o*-benzyloxyphenylglyoxyate occurs by energy transfer to the metal complex.

WE have studied the previously unreported photoisomerization:

$$cis\text{-Cr}^{\text{III}}(\text{fba})_3 \overset{h\nu}{\rightleftharpoons} trans\text{-Cr}^{\text{III}}(\text{fba})_3$$

where fba is the 1,1,1-trifluoro-5,5-dimethylhexane-2,4-dionato-anion. Optically dense solutions of pure *cis*- and pure *trans*-$\text{Cr}^{\text{III}}(\text{fba})_3$ in hexane were irradiated at 253·7 nm, 313 nm, 366 nm, and > 520 nm. The *cis*- and *trans*-isomers resulting from photoreaction were separated by g.l.c., using a silicone column and an electron capture detector (tritium foil).[1,2]

Irradiation in the ligand bands of either *cis*- or *trans*-$\text{Cr}^{\text{III}}(\text{fba})_3$ leads to isomerization approaching a photostationary state $K = trans/cis = 1{\cdot}6 \pm 0{\cdot}2$. Thermal isomerization, either in the presence of organic solvents, benzene and ethanol, or in the gas phase led to similar values for the equilibrium constant. Difficulties in g.l.c. detector reproducibility prevented smaller error limits, but K clearly is of the order of the statistically expected equilibrium ratio of 1·5 and definitely is not significantly smaller than the statistical ratio as is the case with cobalt(III) acetylacetonates.[3]

The initial quantum yield ϕ(*cis* to *trans*) is small, 0·003 ± 0·002 and clearly cannot account for all the energy available to the complex from the absorbed photon. The quantum yield is essentially independent of irradiating wavelength over the ligand region, and no additional reactions were observed at wavelengths as short as 253·7 nm.

The similarity between the photoinduced and thermally induced reactions suggest a common intermediate for the isomerization, presumably some low-lying state of the complex. It is important to note in this regard, however, that direct irradiation of the *d–d* band did not give rise to isomerization or any other detectable reaction.

Solutions containing metal complex and methyl *o*-benzyloxyphenylglyoxylate of such concentrations that 99% of the incident light (313 and 366 nm) was absorbed by the keto-ester, exhibited isomerization of the complex with a quantum yield comparable to that found for direct photoisomerization. The keto-ester photoreaction, however, was quenched by the presence of the metal complex. Methyl *o*-benzyloxyphenylglyoxylate has been studied previously, and convincing evidence that it reacts from the triplet state has been obtained.[4,5] Among the tests run for the nature of the photoreaction of the keto-ester were quenching studies with piperylene, naphthalene, and cyclohexa-1,4-diene. $\text{Cr}^{\text{III}}(\text{fba})_3$ is 4·5, 3·0, and 0·65 as efficient in quenching the keto-ester photoreaction as piperylene, naphthalene, and cyclohexa-1,4-diene, respectively.[5] The coupled observations of triplet quenching and quencher isomerization provide complementary evidence to that of other workers that triplet quenching by Cr^{III} complexes occurs with energy transfer.[6]

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