bonded) except for the hydrogen on the bridging vinyl carbon which was located from a difference Fourier synthesis.

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(15) (a) Local versions of the following programs were used: (1) SYNCOR, W. Schmonsees' program for data reduction; (2) FASTES, E. R. Corey's program for generation of normalized structure factors; (3) REL, R. E. Long's program for phase determination by Sayre's method; (4) FORDAP, A. Zalkin's Fourier Program; (5) ORFLS and ORFFE, W. Busing, K. Martin, and M. Levy's full matrix least-squares program and function and error program; (6) ORTEP, C. K. Johnson's program for drawing crystal models; (7) HFINDR, A. Zalkin's program for calculating idealized hydrogen coordinates. (b) Scattering factors were taken from "The International Tables for X-Ray Crystallography", Vol. IV, J. A. Ibers and W. C. Hamilton, Ed., The Kynoch Press, Birmingham, England, 1974.

Michael J. Albright, William M. Butler, Thomas J. Anderson
Milton D. Glick, John P. Oliver*
Department of Chemistry, Wayne State University
Detroit, Michigan 48202

Received February 24, 1976

Intersystem Crossing in Chromium(III) Photochemistry

Sir:

We have recently suggested[1] that $^4T_{2g} \rightarrow {}^2E_g$ intersystem crossing (ISC) proceeds at a comparable rate to $^4T_{2g}$ vibrational equilibration for the $Cr(en)_3^{3+}$ ion (en = ethylenediamine) in aqueous solution at 25 °C. The conclusion was based in part on the higher phosphorescence yield on 436 nm relative to 514-nm excitation (ϕ_p 514 nm/ϕ_p 436 nm = 0.63). This emission ratio was obtained after correction for the relative lamp intensities at 436 and 514 nm, using absorbance matched $Ru(bpy)_3^{2+}$ solutions as photon counters. We have since independently confirmed the value of this emission ratio (0.66), using ferrioxalate[2] and reinecke's salt[3] actinometry to determine the 436- and 514-nm lamp intensities, respectively.

It is noteworthy that Adamson et al. have previously postulated that ISC may successfully compete with $^4T_{2g}$ equilibration for Cr(III) complexes at very low temperatures.[4-6] They attribute[5,6] the phenomenon to solvent restricted (and therefore temperature dependent) quartet relaxation, associated with the substantial distortion of the equilibrated $^4T_{2g}$ state from ground state geometry. If this explanation also applies at room temperature, it would seriously compromise the widely held contention[7-10] that the photoreactivity of Cr(III) systems of O_h and D_3 symmetry originates solely out of the $^4T_{2g}$ excited level. A critical argument for exclusive quartet reactivity has been the high activation energy observed for Cr(III) phosphorescence in these systems.[7,8] It is apparent that solvent restricted quartet relaxation would provide an alternative explanation for this high activation energy.[6] Therefore, thermal $^2E_g \rightarrow {}^4T_{2g}$ back-ISC *may* not be the principal fate of ^2E_g state molecules, and that part of the overall photoreaction that is quenched upon ^2E_g state quenching may in fact be associated with *direct* reaction out of the doublet level. A doublet reaction component would also be in keeping with recent studies on C_{4v} systems such as $Cr(NH_3)_5NCS^{2+}$ [11] and $Cr(NH_3)_5Cl^{2+}$.[12]

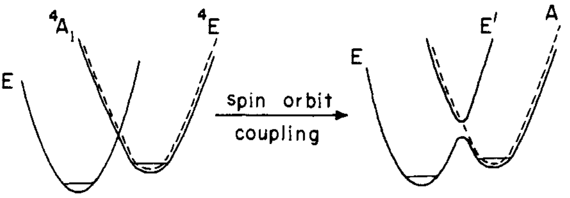

Figure 1.

We present here experimental evidence against solvent restricted quartet relaxation playing an important role in aqueous solution Cr(III) photochemistry near room temperature. The wavelength dependence of the activation energy for phosphorescence has been examined for the species $Cr(en)_3^{3+}$ and $Cr(NH_3)_6^{3+}$, using emission equipment and procedures described elsewhere.[1] Excitation wavelengths of 460 and 514 nm were employed. The former wavelength corresponds to population of the $^4T_{2g}$ state above the anticipated "cross-over point" between the $^4T_{2g}$ and ^2E_g surfaces, whereas 514-nm excitation corresponds to generation of the $^4T_{2g}$ level below the crossing point and near its vibrationally equilibrated configuration.[1,6] For both compounds, no wavelength dependence was observed. Activation energies of 10.5 and 10.3 kcal mol^{-1} were obtained for $Cr(en)_3^{3+}$ on 460- and 514-nm excitation, respectively, while the corresponding values for $Cr(NH_3)_6^{3+}$ were 10.4 and 10.3 kcal mol^{-1}. On the basis of Adamson's "solvent-restricted" model, essentially no activation energy is predicted for the case of 514-nm irradiation. Further, this model requires large and small activation energies for the phosphorescence intensity and lifetime, respectively, on 460-nm excitation. The observation by Ballardini et al.[8] that intensity and lifetime activation energies parallel each other for $Cr(en)_3^{3+}$ is therefore also inconsistent with the model.

In addition, we have investigated the temperature dependence of percent photoracemization quenching of (+)-D-$Cr(en)_3^{3+}$ by hydroxide ion (a selective doublet state-quencher)[1] on 436-nm excitation. Optical rotation measurements were obtained using a Bendix automatic polarimeter (Model 1164). Over the temperature range studied (5–35 °C) percent reaction quenching remained essentially constant (58–60%).[13,14] This is consistent with back-ISC as the principal deactivation mode of doublet molecules, whereas Adamson's hypothesis requires percent quenching to decrease with rising temperature.

On the basis of the foregoing discussion, an alternative explanation must therefore be sought for $^4T_{2g} \rightarrow {}^2E_g$ ISC successfully competing with $^4T_{2g}$ relaxation for $Cr(en)_3^{3+}$ in room temperature solution. Beattie has recently noted[15] in an analysis of Fe^{2+} (d^6) systems, that formally spin-forbidden transitions can occur rapidly along a single potential energy surface (adiabatically) provided the states involved have an irreducible representation in common. For $Cr(en)_3^{3+}$ under D_3 symmetry, the $^4T_{2g}$ level splits into $^4A_1$ and ^4E components. In the presence of strong spin-orbit coupling the spin designations may have limited significance,[16] and the quartet and doublet surfaces have two irreducible representations (E) in common. The noncrossing rule may therefore be invoked[17] as depicted in Figure 1, resulting in a single surface (E) connecting the two potential energy minima. We suggest this then provides a mechanism for ISC to compete with quartet vibrational equilibration.

We note that $Cr(NH_3)_6^{3+}$ also displays a wavelength dependent phosphorescence intensity (ϕ_p) across the first ligand field absorption band with ϕ_p 514 nm/ϕ_p 436 nm = 0.60. As previously discussed for $Cr(en)_3^{3+}$,[1] the observation is consonant with very rapid $^4T_{2g} \rightarrow {}^2E_g$ ISC. (Very rapid ISC has been recently demonstrated for $Cr(NCS)_6^{3-}$ and $Cr(acac)_3^0$ from picosecond flash studies.[21] However, no direct measure of the relative rates of ISC vs. quartet relaxation is possible from such investigations.) Assuming strict O_h symmetry for the $^4T_{2g}$ and ^2E_g states, the quartet and doublet surfaces lack an irreducible representation in common. However, the vibrationally equilibrated $^4T_{2g}$ state is undoubtedly distorted from ground state geometry, C_{4v}, D_{3h}, or D_{5h} symmetry having been suggested.[18-20] For either distortion model, provided the "crossing point" between the quartet and doublet surfaces occurs after substantial quartet relaxation, an irreducible representation (E) is again available to the states involved in ISC. Extension of these studies to other Cr(III) systems holds considerable promise for providing a clearer insight into the details of $^4T_{2g}$ excited state relaxation in aqueous solution.

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N. A. P. Kane-Maguire,* D. E. Richardson, C. G. Toney
Department of Chemistry, Furman University
Greenville, South Carolina 29613
Received September 22, 1975

Carbonyl Compounds as Primary Products in the Reduction of Alkyldioxycobaloximes by Sodium Borohydride

Sir:

Stereochemical studies of oxygen-insertion in the cobalt-carbon bond of alkylcobaloximes have recently been reported.[1-3] The procedure used by Jensen and Kiskis[1,2] consisted in preparing first an optically active cobaloxime from a readily available chiral alkyltosylate and, secondly, in converting the alkyl complex **1** into the corresponding oxygen insertion derivative **2** which was subsequently reduced to the corresponding alcohol **3** by excess sodium borohydride. Obtention of an optically inactive alcohol was considered as a proof of racemization during the oxygen insertion reaction (Scheme I). Shinozaki and Tada[3] reached the same conclusions using a similar method which involved the synthesis of two diastereomeric alkylcobaloximes which were submitted to oxygen insertion and then to $NaBH_4$ reduction.

Table I. Reduction Products of Alkyldioxycobaloximes **2** by $NaBH_4$[a]

		Products, %	
Compounds	Yield, %	R_1COR_2	R_1CHOHR_2
2a	20	100	—
2b	70	60	40
2d	90	100	0
2e	80	100	0
2f	50	100	0
2g	80	50	50

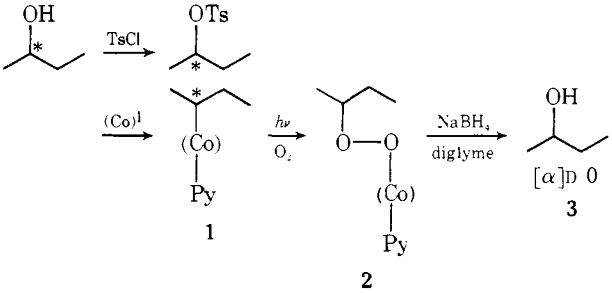
[a] The reductions were carried out using an equivalent amount of $NaBH_4$.

Table II. Evolution of Products during the Reduction of Compound **2d** by $NaBH_4$[a]

t, min	$p\text{-F-}C_6H_4\underset{\substack{\| \\ O}}{C}CH_3$	$p\text{-F-}C_6H_4\underset{\substack{| \\ OH}}{C}HCH_3$
60	33	67
90	20	80
120	0	100

[a] A fivefold excess of $NaBH_4$ was used.

Scheme I



In the present communication, we report preliminary results which establish that the primary products of reduction of alkyldioxycobaloximes by $NaBH_4$ are not the alcohols but, for the main part, the corresponding ketones or aldehydes, which are, but subsequently, reduced to the alcohols by excess $NaBH_4$.

Products **2a–c** were prepared by photochemical oxygenation of the corresponding alkylcobaloximes **1a–c** and purified as previously described.[4] Complexes **2d–h** were obtained by thermal insertion of oxygen into the cobalt-carbon bond of alkylcobaloximes **1d–h** and purified similarly (Scheme II). When methanolic solutions of alkyldioxycobaloximes were treated with equimolecular amounts of $NaBH_4$, the corresponding aldehydes or ketones were isolated (Table I) and characterized by their NMR spectra, or converted into their crystalline 2,4-dinitrophenylhydrazine derivatives.