Photoracemization of Tris(1,10-phenanthroline)chromium(III). Phosphorescence Quenching as a Tool for Identification of Reactive Excited State

Sir:

Although Cr(III) complexes have been the subject of numerous photochemical studies in their ligand field absorption region, debate continues as to relative significance of quartet and doublet excited states as immediate precursors of photoreaction.[1-4] For mixed ligand systems, some quartet involvement is indicated from evidence that individual ligand quantum yields are wavelength dependent. However, such criteria fail for complexes of O_h or D_3 symmetry. We discuss here a promising approach to the general problem of distinction between quartet and doublet precursors to reaction.

Chen and Porter's observation[3] of doublet quenching of Reinecke's salt by $Cr(CN)_6^{3-}$ in fluid solution at −65° without complete reaction quenching provides direct experimental confirmation that reaction may occur from ^4T excited states. The report[5] that room temperature phosphorescence of Cr(III) complexes is a relatively common phenomenon suggests modification of Chen and Porter's technique to more conventional temperatures and solvents. Notably, several complexes of O_h or D_3 symmetry exhibit strong room temperature phosphorescence in aqueous solution.[5] We report here our studies on the tris-1,10-phenanthrolinechromium(III) ion ($Cr(phen)_3^{3+}$).

For this compound photoracemization is the dominant photoreaction in aqueous solution for irradiation wavelengths $\geq$350 nm. Thermal corrections are insignificant and photoaquation yields are several orders of magnitude smaller than isomerization yields. Racemization data on $(+)_{589}Cr(phen)_3Cl_3$ have been obtained under irradiation at 350 nm using a Rayonnet photoreactor and at 457.9 nm using an argon ion laser. Light intensity was gauged by ferrioxalate actinometry. A Perkin-Elmer 141 polarimeter was used for rotation measurements. Emission data were obtained as before.[5] Under 440-nm excitation, emission was observed at 735 nm. This corresponds to the wavelength position of the doublet absorption band[6] and is assigned as doublet phosphorescence. Relative intensities were estimated from the integrated emission band areas.

Both racemization and phosphorescence may be sensitive to the counterion present. From an analysis of such counterion effects on these two processes, taken in conjunction with similar studies on the optically active oxalatobis-1,10-phenanthrolinechromium(III) ion ($(-)_{589}Cr(phen)_2ox^+$), the lowest excited quartet state is implicated as the photoreactive level. The data given are for the chloride salts, since this anion has no observable effect on either racemization or phosphorescence.

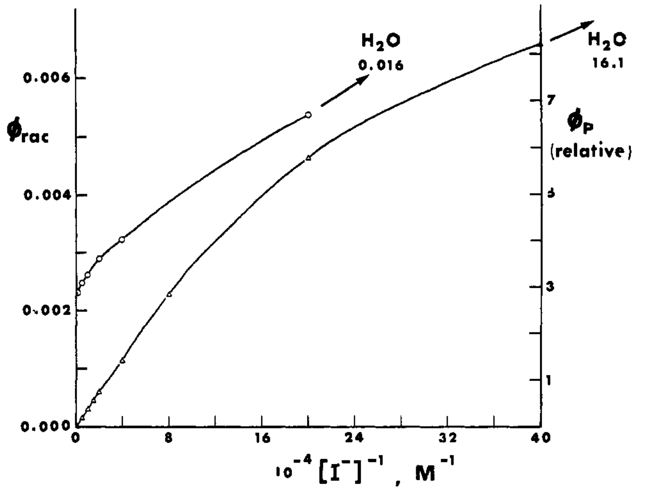

Figure 1. Iodide quenching of photoracemization of $Cr(phen)_3^{3+}$ at 350 nm in aqueous solution at 25° (○) and of $Cr(phen)_3^{3+}$ phosphosphorescence (△).

Photoracemization followed excellent first-order kinetics for greater than 3 half-lives of reaction, the rate constant showing the expected inverse dependence on complex concentration. The racemization quantum yield (ϕ_{rac}) at 25° has been found to be 0.016 at 350 nm and 0.015 at 457.9 nm. The former wavelength corresponds to absorption into a region dominated by strong charge-transfer absorptions, while 457.9 nm is at the long wavelength tail of the lowest spin-allowed quartet band. This implies a value of near unity for the process of conversion between the charge transfer and $^4T_{2g}$ levels. Our data suggest that the quantum yield for phosphorescence (ϕ_p) is several times smaller than that for racemization.[5] It is evident then that radiationless deactivation competes favorably with either photoreaction or radiative decay.

The key observation is that iodide ion quenches both phosphorescence and racemization. The iodide quenching results are shown in Figure 1. While total phosphorescence quenching is achieved at low iodide concentration, ϕ_{rac} is seen to approach a *limiting value* at an iodide concentration above 1×10^{-3} *M*. In fact, 0.14 of the total photoracemization is not quenched by iodide ion. Both the phosphorescence quenching and the quenchable part of the photoracemization follow a Stern–Volmer relationship (ϕ_0/ϕ or $(\phi_0 - \phi_{lim})/(\phi - \phi_{lim})$ *vs.* $[I^-]$ for phosphorescence and racemization, respectively) of slope 4.25×10^5 and 4.45×10^5 M^{-1}, respectively. The quenchable excited state is, most likely, the doublet state. (The iodide quenching can then be rationalized in terms of an external heavy atom effect.) Since 0.86 of the total photoracemization may be quenched, we conclude that 0.86 of reaction occurs from excited molecules that have passed through equilibrated doublet states. The remaining unquenchable 0.14 of the reaction is then attributed to direct racemization from the *lowest excited quartet state*, prior to intersystem crossing to the doublet manifold.

Following Chen and Porter's[3] interpretation, that part of reaction involving the doublet state may proceed either by (a) direct reaction in the doublet or (b) thermal repopulation of the reactive quartet state *via* back intersystem crossing. Several pieces of evidence support

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(5) N. A. P. Kane-Maguire and C. H. Langford, *Chem. Commun.*, 895 (1971).

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the latter pathway for Cr(phen)$_3^{3+}$. Back intersystem crossing will be associated with an activation energy equal to the energy gap between the two states. From a temperature dependence study of photoracemization at 457.9 nm we find that while the nonquenchable or quartet component has an activation energy of 2.2 kcal mol^{-1}, the corresponding value for the quenchable reaction component is 10.1 kcal mol^{-1}. This latter value suggests that radiationless deactivation is a major relaxation mode of the doublet, since experimentally no activation energy would be observed for racemization *via* thermal return if the latter process were the sole fate of the doublet molecules. (Total return would mask the energy requirement for return.) The relatively high efficiency of $^2E_g \rightarrow {}^4A_{2g}$ deactivation may also be inferred from the anomalously low activation energy reported for the phosphorescence intensity of Cr(phen)$_3^{3+}$.[5]

Studies on $(-)_{589}$Cr(phen)$_2$oxCl provide further support for these conclusions. For this system corrections for photoaquation and thermal racemization[7] are again negligible. In aqueous solution at 25° a value of $\phi_{\rm rac}$ of 0.21 is obtained at the wavelengths 350 and 501.7 nm, *i.e.*, a yield 13 times greater than that for Cr(phen)$_3^{3+}$ and in the range[1,2] normally found for Cr(III) photosubstitutions. The very weak emission from this complex precludes a phosphorescence quenching study. However, iodide has no observable effect on $\phi_{\rm rac}$. It appears quite probable then that racemization occurs predominantly through the lowest excited quartet state prior to intersystem crossing. This is in accord with the value of 1.4 kcal mol^{-1} found for the activation energy for this reaction.

The generality of the approach suggested in this communication is illustrated by evidence from OH$^-$ doublet quenching which does not match reaction quenching in the photosubstitution of Cr(NH$_3$)$_6^{3+}$. These results will be reported elsewhere.[8]

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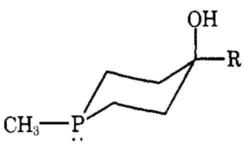
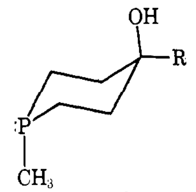
Assignment of Configuration to *cis,trans*-4-Phosphorinanols. X-Ray Analysis of *trans*-1-Methyl-4-*tert*-butyl-4-phosphorinanol[1]

Sir:

From the beginning[2] of conformational study of six-membered cyclic phosphines (phosphorinanes), it was apparent that the system possessed some unique properties. Cis,trans isomers of 1-methyl-4-alkyl-4-phosphorinanols (I) were given tentative structure assignments from nmr spectral differences which suggested that they differed in configuration at phosphorus in their preferred conformations. Further study[3] has not modified this view, but has shown that even

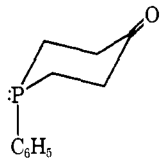


cis-I

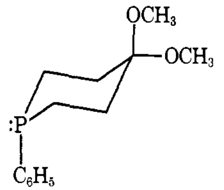


trans-I

in secondary phosphorinanols little preference is expressed by *P*-methyl for either equatorial or axial orientation. That other unusual properties may prevail in this ring system has been made clear from X-ray analysis of some *P*-phenylphosphorinanes (II[4] and III[5]) which were found to have axially oriented phenyl.

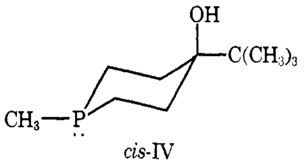


II

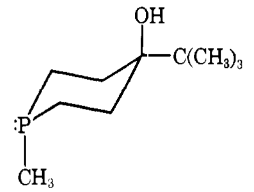


III

It is a matter of considerable importance to the further development of stereochemical understanding of phosphorinanes that unequivocal structural assignments be made among isomer pairs, thus permitting the confident use of spectral differences between isomers for more routine assignments. We here provide unambiguous proof from a single-crystal X-ray analysis for the structure of one of the isomers of IV, both of which are crystalline solids.[3]



cis-IV



trans-IV

The solid which formed in the receiver on distillation of a mixture with composition *ca.* 70% *cis*–30% *trans*-IV had two distinctly different crystalline forms present, and single crystals of each isomer could be identified and separated by microscope examination. One of the isomers crystallizes as well-developed prisms with mp 84–85°, whereas the other forms as thin plates with mp 103–104°. Separation of the isomer mixture by gas chromatography provided specimens with identical melting points. As in earlier studies,[2] the trans structure was assigned to the lower melting isomer, based on the upfield position (δ 0.89) and larger coupling constant ($J_{\rm PCH}$ = 4 Hz) of the PCH$_3$ group relative to the signal from the cis isomer (δ 0.95, $J_{\rm PCH}$ = 2.1 Hz).

A crystal of the more suitable lower melting isomer was selected for X-ray analysis and mounted in a thin-walled capillary under a nitrogen atmosphere. These crystals are monoclinic, space group $P2_1/c$, with eight molecules of C$_{10}$H$_{21}$OP in a unit cell of dimensions *a*

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(1) Supported in part by Public Health Service Research Grant No. CA-05507, National Cancer Institute.

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