undergo both oxidation and reduction reactions.[25] Thus the behavior of *Ru(bpy)$_3^{2+}$ is not without precedent, but the reductive quenching mechanism reported here has not been previously proposed for systems of this kind.

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Registry No. Ru(bpy)$_3^{2+}$, 15158-62-0; Fe(CN)$_6^{4-}$, 13408-63-4; Co(phen)$_3^{2+}$, 16788-34-4; Ru(NH$_3$)$_6^{2+}$, 19052-44-9; Eu(II), 16910-54-6; S$_2$O$_4^{2-}$, 14844-07-6.

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Stereoselectivity in Electron-Transfer Reactions

AIC50607I

Sir:

Despite the vast amount of information available on electron-transfer reactions involving transition metal systems, relatively little is known about possible stereoselectivity in such reactions between pairs of chiral complexes. The use of optically active reagents has generally been restricted to self-exchange reactions, where racemization serves as a convenient monitor of the redox process.[1,2] For example, racemization accompanies self-exchange in aqueous solution between optically inert (+)D-[Co(phen)$_3$]$^{3+}$ and labile [Co(phen)$_3$]$^{2+}$ (phen = 1,10-phenanthroline) and has been implicity attributed to a lack of stereopreference.[3] Paradoxically (+)D-[Co(phen)$_3$]$^{3+}$ was recently reported by Sutter and Hunt[4] to react with labile [Cr(phen)$_3$]$^{2+}$ to yield (−)D-[Cr(phen)$_3$]$^{3+}$. We note that it is possible to rationalize these apparently contradictory results if stereoselectivity is a rather general phenomenon, requiring electron transfer to occur preferentially between reactants of opposite absolute configuration. Although operative, this preference would go undetected in self-exchange reactions—since inversion occurs in both the forward and reverse steps. The model is also consistent with the ΛC_3 and ΔC_3 absolute configurations assigned (+)D-[Co(phen)$_3$]$^{3+}$ and (−)D-[Cr(phen)$_3$]$^{3+}$ from circular dichroism studies.[5] However, in a kinetic study of several redox systems involving non-self-exchange situations, Grossman and Wilkins[6] found no evidence for stereopreference. Inspection of the reactions examined suggests that stereoselectivity may require systems containing π-acceptor ligands (e.g., phen) and/or reductants involving strongly reducing metals (e.g., Cr^{2+}). This model would not specify a particular isomeric preference, although recent NMR studies by La Mar and co-workers[7,8] suggest electron transfer might then be most facile between reactants with the same chirality.

Our research objectives have been to resolve these anomalies and delineate the extent and nature of redox stereospecificity. The initial experiments involved repeating the work of Sutter and Hunt[4] on the (+)D-[Co(phen)$_3$]$^{3+}$ + [Cr(phen)$_3$]$^{2+}$ reaction. Despite numerous attempts, following the experimental procedure outlined by the authors, we have been unable to observe any induction of optical activity in the [Cr(phen)$_3$]$^{3+}$ product. Rotation measurements were recorded at 546 nm immediately after reaction using a Bendix Model 1144 automatic polarimeter with digital readout to ±0.0002°. A small positive rotation was initially observed after reaction, consistent with the slight excess of (+)D-[Co(phen)$_3$]$^{3+}$ employed in each instance. This activity was subsequently lost at a rate consonant with expected [Co(phen)$_3$]$^{2+}$–[Co(phen)$_3$]$^{3+}$ self-exchange. It was verified that [Cr(phen)$_3$]$^{3+}$ is optically stable in the presence of [Co(phen)$_3$]$^{2+}$, using a genuine sample of (+)D-[Cr(phen)$_3$]$^{3+}$.[9] As noted by Sutter and Hunt, the presence of redox stereoselectivity is not a sufficient condition for the experimental observation of the phenomenon. It is also essential that [Cr(phen)$_3$]$^{2+}$ inversion proceed more rapidly than electron transfer. To enhance the probability of this latter condition being met, the reaction was also followed at substantially lower reagent concentrations than those reported. Even when solutions 10^{-4} M in (+)D-[Co(phen)$_3$]$^{3+}$ and [Cr(phen)$_3$]$^{2+}$ were mixed, no resultant induction was observed. Assuming the reported formation of 92% (−)D-[Cr(phen)$_3$]$^{3+}$, a final rotation of −0.067° (5-cm cell 546 mm) was anticipated, a value well within the capabilities of the instrument available. Furthermore, the reaction has been repeated without success at elevated temperatures (up to 70 °C) to take advantage of a probable activation enthalphy difference for the redox and racemization processes. Identical runs carried out at room temperature in 50% ethanol and 50% DMSO met with a similar lack of success. We conclude that the previous communication on this system is most probably in error.[10]

We have extended our present investigation to other outer-sphere redox reactions of the type described. The systems examined are collated in Table I. In no instance was a successful optical induction achieved. Reactions 5–7 provide

Table I. Outer-Sphere Redox Systems Surveyed for Induction of Optical Activity[a]

Reaction	Oxidant	Reductant
1	$(+)_D\text{-}[Co(phen)_3]^{3+}$ [b]	$[Cr(phen)_3]^{2+}$
2	$(+)_D\text{-}[Co(phen)_3]^{3+}$	$[Cr(bpy)_3]^{2+}$
3	$(-)_D\text{-}[Co(bpy)_3]^{3+}$ [c]	$[Cr(phen)_3]^{2+}$
4	$(-)_D\text{-}[Co(bpy)_3]^{3+}$	$[Cr(bpy)_3]^{2+}$
5	$(+)_D\text{-}[Co(phen)_2en]^{3+}$ [d]	$[Cr(phen)_3]^{2+}$
6	$(+)_D\text{-}[Co(phen)(en)_2]^{3+}$ [e]	$[Cr(phen)_3]^{2+}$
7	$(+)_D\text{-}[Co(en)_3]^{3+}$ [f]	$[Cr(phen)_3]^{2+}$
8	$(+)_D\text{-}[Co(phen)_3]^{3+}$	$[Cr(en)_2]^{2+}$ [h]
9	$(+)_D\text{-}[Co(phen)_3]^{3+}$	$[Cr(edta)]^{2-}$ [i]
10	$(+)_D\text{-}[Co(edta)]^{-}$ [g]	$[Cr(phen)_3]^{2+}$
11	$(+)_D\text{-}[Co(edta)]^{-}$	$[Cr(phen)_3]^{2+}$
12	$(+)_D\text{-}[Co(1\text{-}cysu)_3]^{3-}$ [e]	$[Cr(bpy)_3]^{2+}$
13	$(+)_D\text{-}[Co(edta)]^{-}$	$[Cr(edta)]^{2-}$

[a] Equimolar (5×10^{-3} M) solutions of reactants were mixed at 25 °C with the oxidant in slight excess. [b] Reference 9. [c] J. Ferguson, C. J. Hawkins, N. A. P. Kane-Maguire, and H. Lip, *Inorg. Chem.*, 8, 771 (1969). [d] L. S. Dollimore and R. D. Gillard, *J. Chem. Soc., Dalton Trans.*, 369 (1975). [e] L. S. Dollimore and R. D. Gillard, *ibid.*, 933 (1973). [f] J. A. Broomhead, F. P. Dwyer and J. W. Hogarth, *Inorg. Synth.*, 6, 183 (1960). [g] F. P. Dwyer and F. L. Garvan, *ibid.*, 6, 192 (1960). [h] J. H. Balthis and J. C. Bailar, *J. Am. Chem. Soc.*, 58, 1474 (1936). [i] H. Ogino and N. Tanaka, *Bull. Chem. Soc. Jpn.*, 41, 1622 (1968).

a test of the role of π-bonding ligands in the oxidant, while significantly increasing the relative rate of $[Cr(phen)_3]^{2+}$ racemization vs. electron transfer. It is also noteworthy that high-spin $[Cr(en)_2(H_2O)_2]^{2+}$ as reductant in reaction 8 is substantially more labile than low-spin $[Cr(phen)_3]^{2+}$ in reaction 1. Stereospecific effects might also be expected to be more pronounced between reagents of opposed charge, a point examined in reactions 10–12. It is our view that the results of the present study, coupled with the earlier findings of Grossman and Wilkins, provide strong evidence for the general absence of stereospecific effects in outer-sphere redox processes.

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