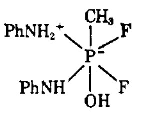

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Stereoselectivity in Electron-Transfer Reactions

Sir:

Previous attempts to observe stereoselectivity in outer-sphere redox reactions have failed. Such asymmetric induction, that is, a rate difference for the reaction of enantiomers with a given chiral compound, has been searched for both by rate studies with separate enantiomers[1] and in competition experiments where racemic mixtures react with a chiral complex.[1,2] In the latter case, searches for deviation from pseudo-first-order kinetics, as one enantiomer preferentially reacts first, and for optical rotation in the final product mixture have been made. These results seem to suggest that, at least in some cases of outer-sphere electron transfer, the reactants are not in contact in the transition state.

In several of these studies, an important factor seems to have been overlooked: that of racemization of any chiral product by electron exchange with its reduced form. For example, $Cr(phen)_3^{2+}$, used as a reductant in several of the experiments, racemizes at 0.123 s^{-1}.[3] The self-exchange rate for $Cr(phen)_3^{3+/2+}$ is not known, but it is undoubtedly close to that of $Cr(bpy)_3^{3+/2+}$ for which 10^7 M^{-1} s^{-1} has been estimated.[4] Thus, even at $Cr(phen)_3^{2+}$ concentrations as small as $\sim 10^{-7}$ M, $Cr(phen)_3^{3+}$ will be kept racemic owing to oxidation by it of racemic $Cr(phen)_3^{2+}$. Asymmetric induction experiments are usually carried out with the net rate of oxidation less than the racemization rate of the reductant. Thus the reductant always presents a racemic mixture, and optically active product may be racemized as quickly as it is formed.

We have investigated some systems that do not suffer from this limitation and have discovered what we believe to be the first cases of stereoselectivity in outer-sphere electron transfer. We will first report results for systems, where, by taking into account the properties of the reactants, we are certain that the reactions are of the outer-sphere type.

In the reaction to be dealt with first, to avoid having to use high concentrations of the chiral oxidant, the reaction was carried out catalytically. The net change involved $S_2O_8^{2-}$ oxidizing $CoEDTA^{2-}$ to $CoEDTA^-$, with $Os(bpy)_3^{3+/2+}$ as the catalyst, according to the sequence

$$\tfrac{1}{2}S_2O_8^{2-} + Os(bpy)_3^{2+} = SO_4^{2-} + Os(bpy)_3^{3+}$$

$$Os(bpy)_3^{3+} + CoEDTA^{2-} = Os(bpy)_3^{2+} + CoEDTA^-$$

Each of these stages is known from independent observations to proceed readily.

A sample of 3.7×10^{-6} M 59% optically pure $[\Delta(-)_{546}Os(bpy)_3](ClO_4)_2$[5,6] was dissolved in a aqueous solution of 8×10^{-4} M $Na_2CoEDTA \cdot 2HClO_4$ with 0.03 N sodium persulfate as oxidant, pH 2.1. Within an hour formation of $CoEDTA^-$ was complete. After cation exchange to isolate the $CoEDTA^-$, CD and optical rotation measurements indicated an optical excess of 2.9 ± 0.3% $\Delta(+)_{546}CoEDTA^-$ [7] or 5.0 ± 0.5% after accounting for the purity of the Os reactant. A sample of the $[\Lambda(+)_{546}Os(bpy)_3](ClO_4)_2$ reacts to produce the $\Lambda(-)_{546}CoEDTA^-$ in the same yield.

In a similar experiment with optically pure $[\Lambda(+)_DRu(bpy)_3](ClO_4)_2$,[8] the product proved to be 0.4 ± 0.2% $(+)_{546}CoEDTA^-$. Preliminary results indicate that $\Delta(-)_DCo(bpy)_3^{3+}$,[9] $\Delta(+)Fe(phen)_3^{3+}$,[10] and $\Lambda(-)Fe(bpy)_3^{3+}$ [11] react stereoselectively with $CoEDTA^{2-}$ to give several percent optically pure (+)-, (−)-, and $(+)_{546}CoEDTA^-$, respectively, but the results with this group of oxidants are difficult to quantify owing to racemization of the oxidant. It should be noted that no general trend emerges, since, in the cases of $Os(bpy)_3$ and $Co(bpy)_3$, the Δ forms lead to preference for $\Delta(+)_{546}CoEDTA^-$, while it is the Λ forms of $Ru(bpy)_3$, $Fe(bpy)_3$, and $Fe(phen)_3$ that do so. Also, the amounts of induction are all rather small. The 5.0% induction for $Os(bpy)_3^{3+}$ means that the rate ratio is only 52.5/47.5 or 1.11 between the Δ and Λ forms of reductant, corresponding to a difference in activation free energy of ~50 cal/mol.

In addition to these results, we have also noted stereoselectivity in the reaction of $K[(+)_{546}CoEDTA]$[12] with excess $Co(en)_3^{2+}$, but here, because of the lability of Co(II)en complex, we cannot be as certain as in the systems already described, that the reaction is of the outer-sphere type. When 4.7×10^{-4} M $K[(+)_{546}CoEDTA]$ is added to a deaerated solution of 8.2×10^{-3} M $Co(ClO_4)_2$ in 9.6×10^{-2} M ethylenediamine, and the solution acidified after reaction, stoichiometric production of $Co(en)_3^{3+}$ is observed. CD and optical rotation analyses of the product solution indicate an optical purity of 10 ± 2% $\Delta(+)_DCo(en)_3^{3+}$.[13]

A significant enhancement of the extent of discrimination is observed in a nonprotic solvent. When 2.4×10^{-3} M $K[(+)_{546}CoEDTA]$ reacts with 0.2 M ethylenediamine and 5.2×10^{-3} M $Co(ClO_4) \cdot 6H_2O$ in Me_2SO, an optical excess of $(1.1 \pm 0.2) \times 10^{-3}$ M $(+)_DCo(en)_3^{3+}$ is observed, or 46 ± 8% with respect to the added oxidant. These results correspond to relative rates of reaction of the Δ:Λ of $Co(en)_3^{2+}$ with $\Delta CoEDTA^-$ of ~1.2 in the aqueous system and 2.7 in Me_2SO. Particularly for the reaction in Me_2SO, it is difficult to understand the extent of chiral discrimination if several solvent molecules are interposed between the reactants in the activated complex.

Proof that the reaction of $CoEDTA^-$ with $Co(en)_3^{2+}$ proceeds by an outer-sphere path is of critical importance, since asymmetric induction in electron transfer implies that the reactants are in intimate contact, a foregone conclusion for some inner-sphere, but not outer-sphere, electron-transfer reactions.

Rate studies at 30.0 °C, $\mu = 0.14$, have shown that the reaction of $CoEDTA^-$ with $Co(en)_3^{2+}$ follows second-order kinetics with a rate constant of 17 ± 2 M^{-1} s^{-1} ([en] = 0.56 M). Stopped-flow studies show that $Co(en)_3^{3+}$ is produced as fast as $CoEDTA^-$ disappears, within 100 ms of the start of the reaction, and we have been unable to detect an intermediate. As a result, we can estimate that any intermediate must be decomposing at >0.8 s^{-1} at 30 °C.

If the reaction were proceeding by an inner-sphere mechanism, the intermediate would be a $Co^{III}(en)_3$-$EDTACo^{II}$ species, with the Co^{III} bound to five nitrogens and one oxygen. This species would have to decompose to $Co(en)_3^{3+}$ at >0.8 s^{-1}. By way of analogy, $Co(NH_3)_5OAc^{2+}$ in ethylenediamine was found to decompose with a half-life of ~30 min to what appeared to be $[Co(NH_3)_5en]^{3+}$.

It is interesting to note that the results just described can account for the curious "substitution" of ethylenediamine onto $CoEDTA^-$. Dwyer et al.[14] observed that adding KCoEDTA to 50% en at 30 °C yields $Co(en)_3^{3+}$ in several minutes with "partial retention of configuration." Busch et al.[15] studied the reaction further, noting that, from $(+)_{546}CoEDTA^-$, 13.2%

optically pure $(+)_D Co(en)_3^{3+}$ is produced in 50% en and 26% pure in 100% en. They tried to explain these results in terms of a mechanism involving direct substitution of a complex nature. However, we feel the data are better explained in terms of electron-transfer catalysis by $Co(en)_3^{2+}$. Busch et al. noted, in fact, that some Co^{II} is produced when KCoEDTA is dissolved in ethylenediamine.

When KCoEDTA was dissolved in 50% en, we found, in accord with the previous work, the production of $Co(en)_3^{3+}$ within a short time. However, in the presence of added H_2O_2 or EDTA, the reaction did not proceed significantly in several hours. Moreover, added $Co(ClO_4)_2$ accelerated the reaction.

Thus we propose the mechanism

$$CoEDTA^- + Co(en)_3^{2+} \rightarrow Co(en)_3^{3+} + CoEDTA^{2-} \quad (1)$$

$$CoEDTA^{2-} + 3en \rightarrow Co(en)_3^{2+} + EDTA^{4-} \quad (2)$$

Note that only $\sim 1 \times 10^{-4}$ M Co^{II} is necessary for a 5-minute half life. The stereoselectivity demonstrated for reaction 1 leads to the stereoselectivity of the overall reaction.

It remains to be learned whether significant discrimination will be observed in systems where both reactants carry charges of the same sign.

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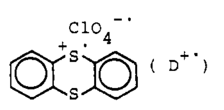
Formation of Sulfinyl Oxide and Singlet Oxygen in the Reaction of Thianthrene Cation Radical and Superoxide Ion

Sir:

Recently much attention has been focussed on photooxygenation via a non-singlet-oxygen mechanism.[1] Some of the cases have been suggested to involve an electron-transfer process to produce the substrate cation radicals and/or superoxide ion in photosensitized oxygenation with α diketones,[1,2] Rose Bengal,[3] or 9,10-dicyanoanthracene (DCA).[4] Foote has originally proposed that the oxidation proceeds through the direct coupling of substrate cation radicals and the superoxide ion.[5] This sequence was applied to the DCA-sensitized oxygenation of alkenes and sulfides.[4a] However, it seems to us that these ion radicals may undergo annihilation by electron transfer from the superoxide ion to cation radicals to produce singlet oxygen which gives indirect oxidized products rather than direct coupling to produce dioxetanes or peroxy intermediates (eq 1).[6,7]

$$D^{+\cdot} + O_2^{-\cdot} \rightarrow \begin{cases} DO_2 \\ D + {}^1O_2 \end{cases} \quad (1)$$



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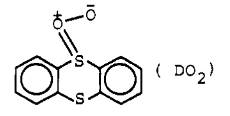

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On the other hand, more recently, Tang[8] and Landis[9] have proposed a new route for non-singlet-oxygen photooxygenation, in which the cation radical reacts with triplet oxygen and propagates radical-chain oxidation for the Barton's reagent[10] catalyzed oxygenation of dienes, such as ergosteryl acetate, and for the photosensitized oxygenation of azines, respectively. Especially, the former case is clearer because of definite implication of cation radicals in the reaction system.

Therefore, to elucidate the possibilities of the oxidation through direct coupling of the cation radical and superoxide ion, it is necessary to use both stable ion radicals. Now this communication reports the first example in which the reaction of the sulfur cation radical and superoxide anion radical gave, not only singlet oxygen by the annihilation reaction, but also direct coupling.

We initiated our investigation using the thianthrene cation radical perchlorate (**1**)[11] and KO_2 as the superoxide anion radical. The reaction of **1** and KO_2 to give sulfinyl oxide (**2**)[12] is evidenced by the change in products as a function of added diphenyl sulfide, which was the original method used by Foote[12a] and Martin.[12c] In a typical experiment, 1-2 mmol of **1** and 4 mmol of KO_2 in 50 cm^3 of acetonitrile were added to the freeze-pump-thaw flask, separately, and the flask was evacuated. The solution of **1** was then transferred into the suspension of KO_2. The color of the solution of **1** (violet, λ_{max} 546 nm) soon disappeared with vigorous evolution of oxygen. The evolved oxygen was measured by manometer and the reaction mixture was analyzed by GLC. Two products, thianthrene and thianthrene 5-oxide, were obtained in comparable yields, but thianthrene 5,5-dioxide unexpectedly was not detected. Treatment of an acetonitrile solution of 20 mmol of diphenyl sulfide and 4 mmol of KO_2 with a solution of 1 mmol of **1** rapidly gave 17% diphenyl sulfoxide with a comparable yield of thianthrene 5-oxide. Parallel studies with Na_2O_2 were also carried out under similar conditions. The yields of thianthrene 5-oxide were half of those in the absence of diphenyl sulfide (see Table I).

Reference to Table I indicates that, at least from a stoichiometric viewpoint, both the annihilation and direct coupling reactions occur. If the annihilation prevails, thianthrene and oxygen may be produced in quantitative yields. In the presence of diphenyl sulfide, thianthrene 5-oxide formation is apparently suppressed (entry III and V), and the yield of thianthrene is concomitantly increased. Furthermore, the yields of thianthrene 5-oxide and diphenyl sulfoxide are approximately equal. Under these conditions, **1** is inert to oxygen, and thianthrene and diphenyl sulfide are not oxidized with KO_2 or Na_2O_2. These results could be explained in terms of complete interception of sulfinyl oxide **2** by diphenyl sulfide. The mechanism is outlined in Scheme I. Hence, the reaction of **2** with thianthrene obtained from the annihilation reaction was readily diverted by diphenyl sulfide. The intermediate **2** was also produced by the reaction of peroxide ion (O_2^{2-}) with **1**, but the

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