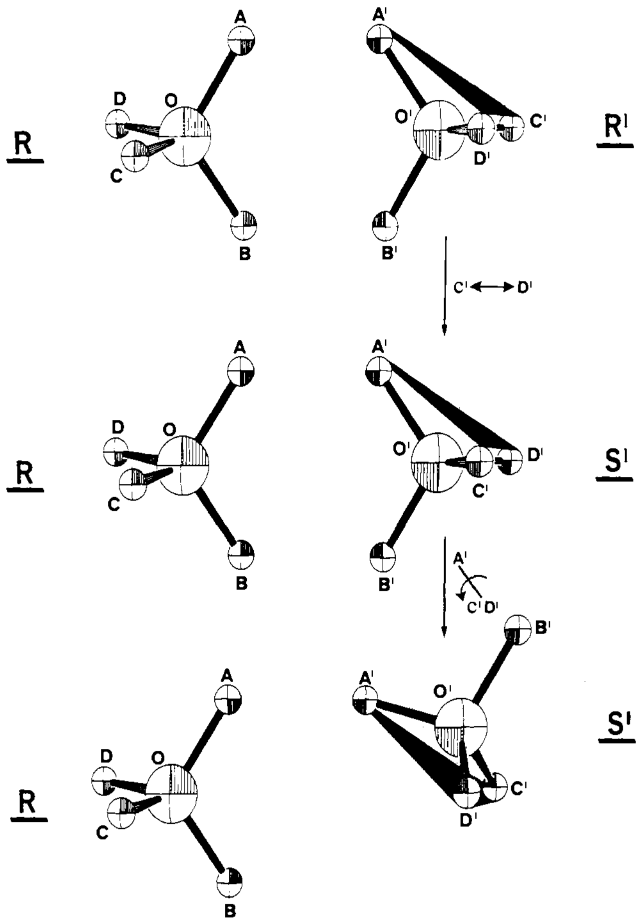

Figure 1. Transformation of *RR′* into *RS′* to show the equal interactions of *R* with the A′C′D′ faces of *R′* and *S′*.

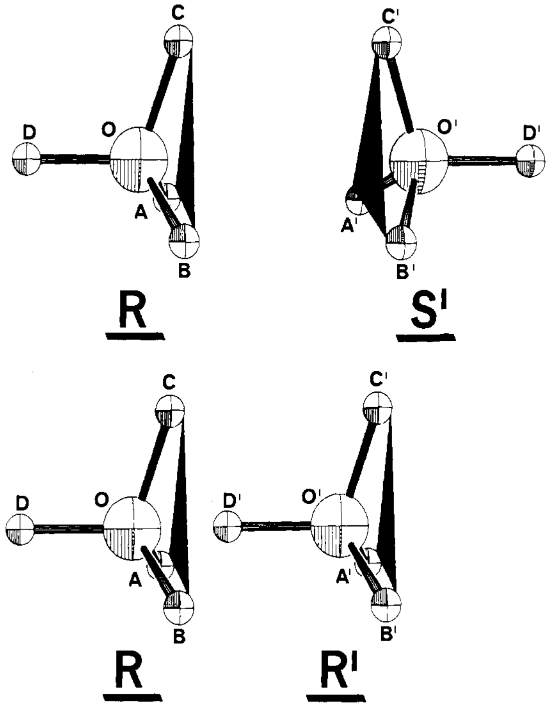

Figure 2. An example of chiral discrimination using the three-contact-point model which is based on eight-center (not six-center) interactions.

and *RR′* complexes shown (shaded triangles), the three-contact-point model excludes this RR′ structure due to the unacceptable steric interactions involving D′, and thereby provides for chiral discrimination. This *RR′* structure is excluded because of eight-center interactions! In a high-temperature limit these eight-center terms will be very different, i.e., chirality effects are due to eight-, not six-, center interactions. Alternatively, when only six centers are considered, the *RR′* and *RS′* structures are energetically equivalent. Again, this cancellation of six-center terms occurs for different OO′ distances in *RR′* and *RS′*. By requiring the same OO′ distances as Salem et al. have done, some of the necessary structures of the complexes would be precluded, which, while physically reasonable, is nevertheless an eight-center effect.

Finally, we have numerically verified the equivalence of the six-center interactions using five different interaction energy expressions, including one which Salem et al. claimed would contribute to chiral recognition.[2]

Supplementary Material Available: Sample results demonstrating the equivalence of six-center interactions using various energy expressions (2 pages). Ordering information is given on any current masthead page.

Magnetic Field Effects in Cobalt(II)-Catalyzed Oxidations: The Role of Electron Spin Angular Momentum

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Magnetic field effects are associated with reaction steps that involve a net change in total angular momentum.[1] We report that an applied magnetic field can influence the rate of a reaction catalyzed by high- and low-spin cobalt(II) complexes in profoundly different ways. The relative rate,[2] *k*(rel), of the O_2 oxidation of 2,6-dimethylphenol to form 2,6-dimethyl-1,4-benzoquinone catalyzed by high- and low-spin cobalt(II) is shown in Figure 1. The high-spin cobalt complex, cobalt(II) bis(3-(salicylideneamino)-propyl)methylamine, Co^{II}SMDPT ($S = {}^3/_2$), has a maximum *increase* in the initial reaction rate at ≃1000 G, while the low-spin cobalt complex, cobalt(II) *N,N′*-bis(salicylidene)ethylenediamine, Co^{II}SALEN ($S = {}^1/_2$), in a 1:10 ratio with pyridine,[3] has a maximum *decrease* in the initial oxidation rate at ≃800 G. Since the electron spin multiplicity of the transition-metal ion results in a different net change in angular momentum in these reactions, it appears high- and low-spin cobalt(II) ions can determine whether an applied magnetic field increases or decreases the initial reaction rate. This could lead to a new approach for the in situ investigation of catalytic reactions.

The leading proposed mechanism[4] for the catalytic oxidation of 2,6-dimethylphenol by cobalt(II) Schiff-base complexes is presented in Figure 2. The magnetic field effect in this reaction has been ascribed[5] to the catalyst regeneration step (f) which

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(1) Atkins, P. W. *Chem. Brit.* **1976**, 214.

(2) The relative rate, *k*(rel), is the initial rate at magnetic field (*H*) divided by the initial rate at zero magnetic field approximated by the earth's magnetic field of ≃0.5 G. All values of *k*(rel) correspond to two standard deviations of the data, ±0.15 for CoSMDPT and ±0.08 for CoSALEN. At zero magnetic field the initial rate of phenol oxidation is 3.30×10^{-2} and 1.19×10^{-1} M^{-1} s^{-1} with CoSMDPT and 1:10 CoSALEN–pyridine, respectively.

(3) Perito, R. P.; Drago, R. S.; Corden, B. B., submitted for publication.

(4) (a) Corden, B. B.; Drago, R. S.; Perito, R. P. *J. Am. Chem. Soc.* **1985**, *107*, 2903. (b) Zombeck, A.; Drago, R. S.; Corden, B. B.; Gaul, J. H. *J. Am. Chem. Soc.* **1981**, *103*, 7580 and references therein; (c) Bedell, S. A.; Martell, A. E. *J. Am. Chem. Soc.* **1985**, *107*, 7909, and references therein.

(5) (a) Perito, R. P.; Corden, B. B. *J. Am. Chem. Soc.* **1987**, *109*, 4418. (b) Perito, R. P.; Corden, B. B. *J. Am. Chem. Soc.* **1988**, *110*, 3472. (c) Perito, R. P.; Corden, B. B. *Inorg. Chem.* **1988**, *27*, 1276. (d) Paquin, J.; Corden, B. B., submitted for publication. The electron spin multiplicity of cobalt(II) can only influence steps (a), (c), and (f). Observation of steric effects by the substituent phenol rules out step (a) as responsible for the observed magnetic field effects [5d]; the initiation step (c) can be ruled out because it exhibits no mass or magnetic kinetic ^{2}H isotope effect with 2,6-$(tBu)_2$-phenol-OD although a kinetic mass and magnetic isotope effect is observed with 2,6-$(tBu)_2$-phenol-4-d_1-OD [5b].

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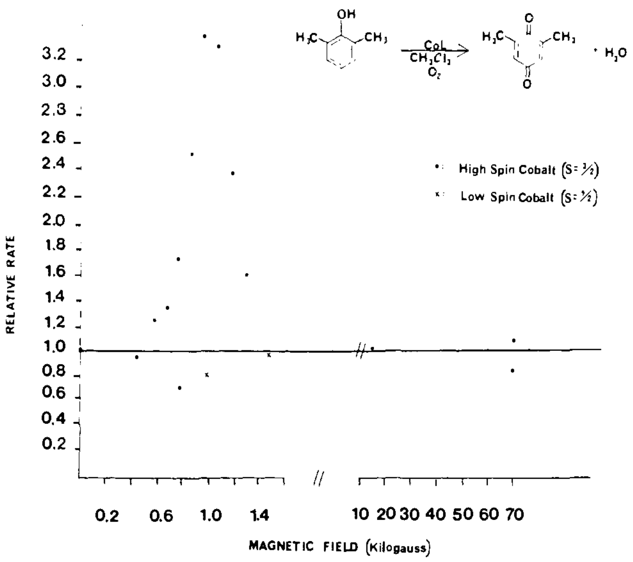

Figure 1. The effect of a magnetic field on the relative rate, *k*(rel), in the catalytic oxidation of 2,6-dimethylphenol by high spin CoSMDPT ($S = {}^3/_2$) and low spin Co(SALEN)(py) ($S = {}^1/_2$).

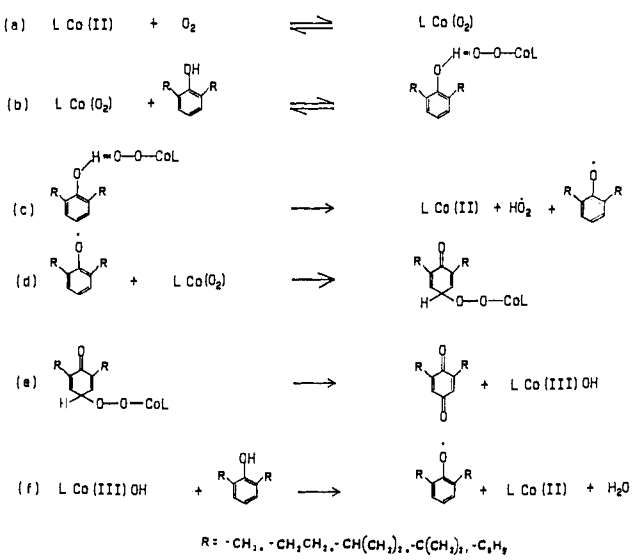

Figure 2. A mechanistic scheme for the catalytic oxidation of 2,6-dimethylphenol by a cobalt(II) Schiff-base complex. L constitutes five of the donor atoms in SMDPT or SALEN(py).

involves electron transfer between two diamagnetic species, $LCo^{III}OH$ and 2,6-dimethylphenol. Since the formation of the phenoxy radical ($S = {}^1/_2$), $Co^{II}SALEN(py)$ ($S = {}^1/_2$) or $Co^{II}SMDPT$ ($S = {}^3/_2$), and H_2O involves a different net change in electron spin angular momentum, it is not unreasonable to expect different magnetic field effects.

The *k*(rel) versus H profile in Figure 1 indicates that the magnetic field effect in these reactions is the consequence of at least two mechanisms which manifest opposite magnetic field effects.[6] One mechanism involves an electronic Zeeman effect which induces mixing between states with different electron spin multiplicities. It is proportional to the magnetic field strength and Δg, the difference in the g values of the unpaired electrons in the reaction pair. This effect is balanced by a hyperfine coupling mechanism which is most effective when $H = -2J/\Delta g\beta$, where $-2J$ is the electron spin–spin coupling and β is the electronic Bohr magneton. The magnetic field effects for the high- and low-spin cobalt(II) catalysts is the sum of the relative contributions of these two intersystem crossing processes which occur during the electron-transfer step (f).

The difference in the magnetokinetics of high-spin $Co^{II}SMDPT$ and low-spin $Co^{II}SALEN$ can be understood from existing theory developed to interpret magnetic field effects in singlet–triplet (S–T) radical pair[6] and triplet–triplet (T–T) annihilation reactions.[7] The catalyst regeneration step (f) is thought to involve the initial encounter of diamagnetic $LCo^{III}OH$ and 2,6-dimethylphenol, the transfer of an electron to form a singlet state radical pair, followed by intersystem crossing to produce the products, H_2O, LCo^{II}, and the phenoxy radical. The back reaction is spin forbidden once intersystem crossing to an electronic state with higher spin multiplicity has occurred. It follows that for $Co^{II}SALEN$, where a weak magnetic field inhibits the formation of the triplet state products, the transmission coefficient for step (f) is influenced by the rate of intersystem crossing between the singlet and triplet states, a rate that depends upon the degree of S–T mixing in the low-spin cobalt(II)–phenoxy radical pair. In contrast, $Co^{II}SMDPT$ accelerates the reaction rate in a weak magnetic field. Because a high spin cobalt(II)–phenoxy radical forms a quintet–triplet state pair,[8] quantum mechanical mixing with a singlet state potential energy surface further along the reaction coordinate is precluded. We believe the difference in the magnetokinetics of high- and low-spin cobalt(II) complexes is explained in these terms.

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Dynamics of an Oxazole Compound Bound to a Common Cold Virus

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Due to the recent availability of crystal structures for one of the human rhinoviruses, HRV-14, with and without synthetic antiviral compounds bound to the protein coat,[1] it has become feasible to consider some of the macroscopic consequences of the binding of antivirals in terms of models of the microscopic interactions[2] and dynamics.[3] In this report, we focus on whether the dynamics of the antiviral drug itself when bound to the virial coat proteins are weakly coupled or strongly coupled to the dynamics of the protein and how this coupling is achieved. The oxazole antiviral compound we consider is 5-[7-[4-[(4,5-dihydro-4-methyl-2-oxazolyl)phenoxy]heptyl]-3-methylisoxazole. The results of our investigations may have implications for both

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