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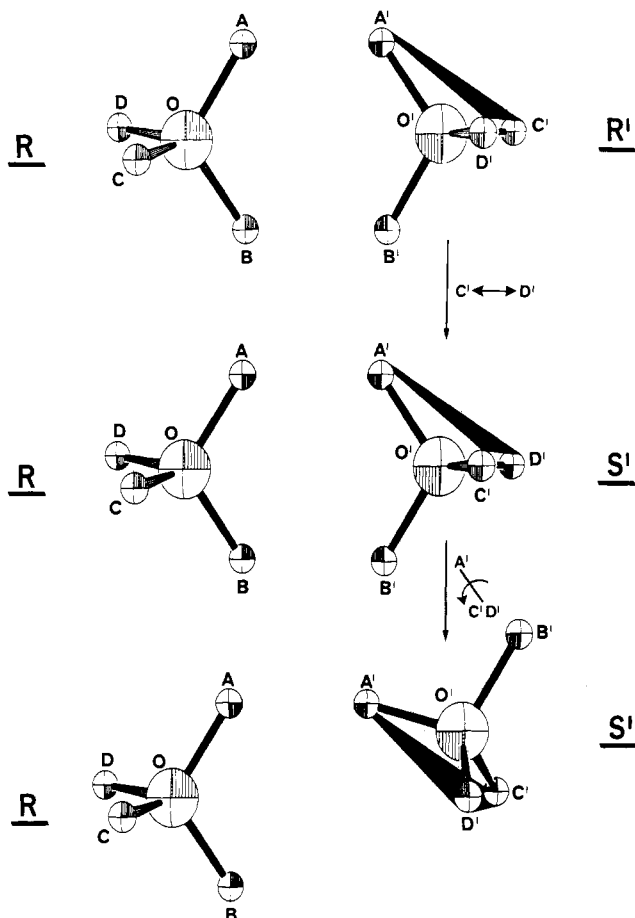


Figure 1. Transformation of RR' into RS' to show the equal interactions of R with the $A'C'D'$ faces of R' and S' .

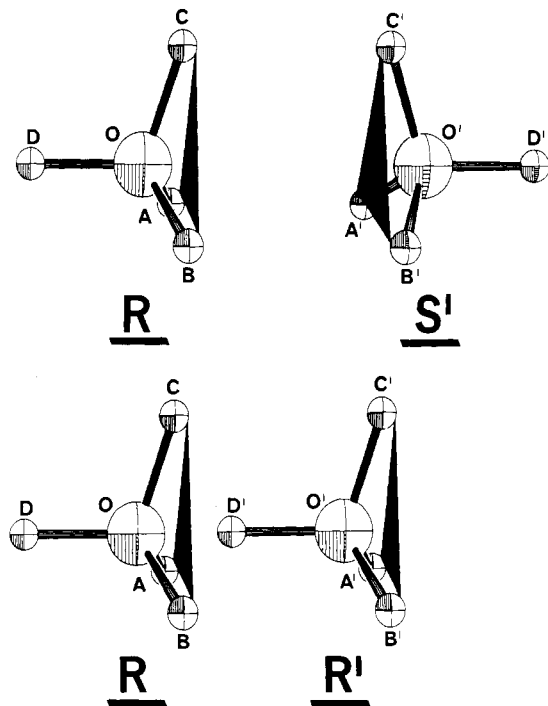


Figure 2. An example of chiral discrimination using the three-contact-point model which is based on eight-center (not six-center) interactions.

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, $k(\text{rel})$, 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, $\text{Co}^{\text{II}}\text{SMDPT}$ ($S = 3/2$), 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, $\text{Co}^{\text{II}}\text{SALEN}$ ($S = 1/2$), 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 mechanism⁴ 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 ascribed⁵ to the catalyst regeneration step (f) which

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

(2) The relative rate, $k(\text{rel})$, 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 $k(\text{rel})$ 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 $1.19 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$ 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 ^2H isotope effect with 2,6-($t\text{Bu}$)₂-phenol-OD although a kinetic mass and magnetic isotope effect is observed with 2,6-($t\text{Bu}$)₂-phenol-4- d_1 -OD [5b].