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Supplementary Material Available: Tables of selected bond distances, bond angles, positional parameters, and thermal parameters (4 pages); tables of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Magnetic Field Effects on the Catalytic Oxidation of 2,6-Di-*tert*-butylphenol

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Although magnetic field effects in photochemical processes are well documented,[1] similar claims of magnetic perturbations on thermal reactions and biological processes suffer from irreproducibility and flawed experimental design or originate from controversial mechanisms.[2] Recent observations of CIDNP spectra in organometallic reactions indicate that radical pair formation can occur.[3a,b] We report a catalytic thermal reaction altered significantly by a laboratory magnetic field.

An applied magnetic field alters the oxidation rate of 2,6-di-*tert*-butylphenol to the corresponding benzoquinone (BQ) or diphenoquinone (DPQ) in the presence of dioxygen and a transition-metal catalyst. Reaction conditions are adjusted so that cobalt(II)bis(3-(salicylideneamino)propyl)methylamine, Co(SMDPT) ($S = {}^3/_2$), generates only BQ[4] while manganese(II)-bis(3-((5-nitrosalicylidene)amino)propyl)methylamine, Mn(5-NO$_2$SMDPT) ($S = {}^5/_2$), forms only DPQ.[5] Two stock solutions were prepared immediately prior to the experiment, one containing 2,6-di-*tert*-butylphenol (DTBP) in CH_2Cl_2 and the other with the catalyst in deoxygenated CH_2Cl_2. The DTBP stock solution (0.1 mL) was syringed into a 5-mm screw cap NMR tube followed by the syringe addition of the catalyst solution (0.1 mL). Pure dioxygen was bubbled through the solution for 2 min, and the tube was sealed and placed in an air-driven turbine spinner to agitate the solution to ensure that mass transfer of O_2 into the solution is not rate limiting. An external magnetic field[6] is applied by placing the entire sample volume midway between and at the center of the 4-in. pole faces of an electromagnet. The 70.05 kG field was obtained from the superconducting magnet of a 300-Mhz Bruker NMR spectrometer. Dioxygen and DTBP are present in sufficient concentration to ensure that the rate of product formation is linear during the reaction interval, and reaction conditions were chosen to prevent formation of a precipitate.[7] The

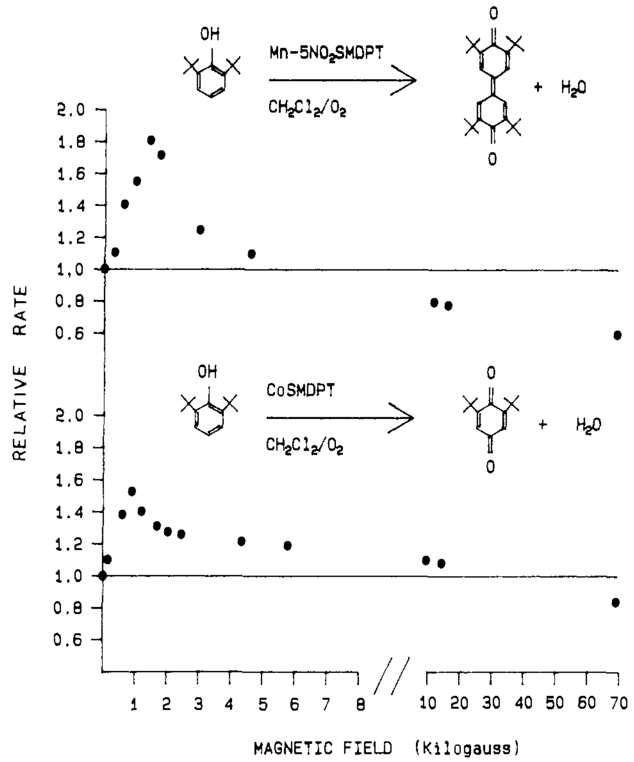

Figure 1. Relative rate of substrate oxidation vs. magnetic field strength (H). The initial rate at field H is divided by the initial rate at zero magnetic field.

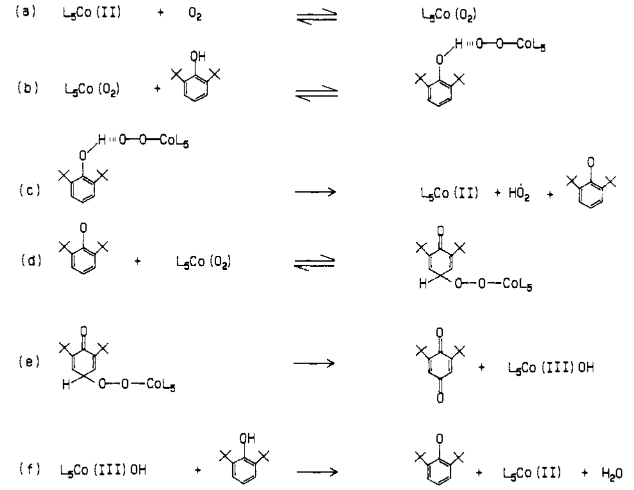

Figure 2. Mechanism of DTBP oxidation by CoSMDPT in the presence of O_2.

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[6] Magnetic field strength (H, Oe) corresponds to magnetic inductance (H, G). Zero-field is approximated by the earth's field of 0.5 G.

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temperature (25.0 ± 1.0 °C) was regulated by a Varian temperature controller interfaced to an air-flow system. The product yield was obtained by NMR integration of the *tert*-butyl resonances of DTBP and BQ or DPQ.[8] The reproducibility of the reaction was within NMR integration error limits (±3%).[9]

Figure 1 illustrates the effect of a magnetic field on the relative rate, k(rel), of the catalytic oxidation of DTBP. The relative rate is the ratio of the rate at magnetic field (H) to the rate at zero-field. The complicated k(rel) vs. magnetic field strength profile in Figure 1 is analogous to photochemical investigations where the magnetic field alters the intersystem crossing rate between a triplet radical pair and a singlet state product.[1] The observed dependence of k(rel) is between a maximum value of 2.0 in a weak magnetic field and a minimum of $^1/_3$ in an infinite magnetic field.[1,10,11] By use of the procedure developed by Doubleday and Turro, the relative contribution of spin–orbit (SOC) and hyperfine coupling (HFC) to intersystem crossing can be determined.[1c,d] If it is assumed that a radical pair reaction is responsible for the observed magnetochemistry, the ratio of SOC to HFC is estimated to be 77/23 ($H = 0$), 65/35 ($H = 1000$), and 92/8 ($H = 7.0 \times 10^4$) for the cobalt-catalyzed oxidation and 53/47 ($H = 0$), 15/85 ($H = 1390$), and 84/16 ($H = 7.0 \times 10^4$) for the manganese-catalyzed oxidation. As the separation between the unpaired electron spins in a triplet radical pair increases, the contribution from the magnetic field dependent HFC process increases.[11a,b] Spin-sorting reactions involving higher spin states will exhibit a similar trend between electron spin separation distance and the range in k(rel).[11c]

The proposed mechanism[4b,c] of the cobalt-catalyzed oxidation of DTBP is illustrated in Figure 2. In principle, any process that alters the concentration of the active catalyst, Co(*S*MDPT)(O_2) ($S = {}^1/_2$) (steps a and f of Figure 2), the phenoxy radical concentration (steps c and f), or the rate-determining step (step d or e)[4a] will affect the reaction rate. Step a can be eliminated from consideration because its forward rate constant is reported to be on the order of $k = 3.4 \times 10^3$,[12] $>10^5$ times faster than the rate-determining step. Moreover, a 10 000-G magnetic field imparts only a fraction of a kilocalorie to the free energy of the equilibrium. Step b involves the hydrogen bonding of the substrate to the catalyst[13] and cannot be responsible for the spin-sorting process observed. The importance of step c was tested by examining DTBP deuteriated in the phenol position. Since the nuclear magnetic moment of ^{2}H is smaller than ^{1}H,[14] the HFC process will be less efficient if step c contributes to the observed effects. The oxidation rate of deuteriated DTBP–OD by either catalyst is within experimental error limits (±3%) of the DTBP–OH rate at $H \geq 0$. Hence, steps a–c are not implicated in the observed magnetic field effect. On the other hand, steps d–f might be responsible for the observed magnetic field effect. Either step d or step e can be interpreted as rate limiting,[4a] and both could involve a spin-sorting process. Step d describes the approach of two doublet molecules to form a radical pair that combines to form the metal peroxide.[4a] If subsequent decomposition of the metal peroxide to BQ and diamagnetic-oxidized catalyst involves homolytic bond cleavage, then step e could be influenced by a magnetic field. Finally, the perturbation of step f, the rate of catalyst regeneration, can alter the reaction rate by changing the steady-state concentration of the phenoxy radical. Therefore, steps d–f singly or collectively can be responsible for the magnetic field behavior.

The fact that Mn(5-NO_2*S*MDPT) and Co(SMDPT) exhibit similar magnetic field effects provides circumstantial evidence that step f is influenced. Mn(5-NO_2*S*MDPT) rapidly converts to the dimer, [Mn(5-NO_2SMDPT)]$_2$O$_2$ ($S = 2$),[5d] in the presence of O_2 and a proton source,[5] and this species generates phenoxy radicals which result in the formation of the coupled quinone, DPQ. Since the manganese catalyst does not form BQ, it appears unlikely that steps d or e in the cobalt-catalyzed oxidation are responsible for the magnetic effect. The manganese-catalyzed reaction exhibits a greater magnetic field effect than cobalt due to the increased importance of HFC.[11c] This is consistent with a manganese dimer and a cobalt monomer catalyst, since the greater separation between the unpaired electron spins in a triplet radical pair is expected for a dimer.

Previous investigations of magnetochemistry have focused on stoichiometric reactions where a triplet radical pair forms both cage and escape products. These reactions often exhibit a magnetically induced change in cage product yield between 5% and 15%.[1,2,10] In certain cases, the reported change is comparable to the error limits. In contrast, the Mn(5-NO_2*S*MDPT)-catalyzed oxidation produces a 27% change in product yield (1390 vs. 70 050G). Hence, the cumulative effect of long-term exposure to relatively weak magnetic fields could be observable because the rate of enzymatic reactions might be altered. The implication of this environmental effect on biochemically significant processes has yet to be investigated adequately.[2i]

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(7) Initial concentrations are DTBP (4.85×10^{-1} M) and either Co*S*MDPT or Mn(5-NO_2*S*MDPT) (8.1×10^{-3} M). The cobalt- and manganese-catalyzed reactions were measured after 36 and 23 h, respectively. Integration of the NMR spectrum requires 10 min and is insignificant compared to the total reaction time. In the case of Co*S*MDPT, formation of DPQ begins to be evident by 41 h. This product is formed by decomposed catalyst, and the rate of DPQ production increases as the catalyst decomposes. The rate of BQ formation catalyzed by Co*S*MDPT and of DPQ by Mn(5-NO_2*S*MDPT) is linear during the initial 36 and 23 h, respectively, and is a good estimate of the initial rate. Initial rates at zero-field are $k(\mathrm{Co}) = 1.2 \times 10^{-2}$ and $k(\mathrm{Mn}) = 1.8 \times 10^{-2}$ M^{-1} s^{-1}.

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(9) NMR integration compares favorably (±5%) to an alternative workup procedure where the reaction mixture was quenched immediately by its addition to a silica gel column and chromatographed with CH_2Cl_2. The product concentration was analyzed by its visible spectrum (quinone, ϵ_{315} 6.58×10^2 M^{-1} cm^{-1}; diphenoquinone, ϵ_{425} 7.64×10^4 M^{-1} cm^{-1}).

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Phospholipid Membranes from a Polymeric Phosphatidylcholine[†,1]

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In this report we show that a preformed phospholipid polymer (**2**), derived from 1,2-bis(2-mercaptohexadecanoyl)-*sn*-glycero-3-phosphocholine (**1**),[3] readily assembles into monolayer and bilayer membranes which (i) retain a natural phosphatidylcholine surface, (ii) display a phase transition, and (iii) exhibit compressibility behavior which is nearly identical with that of their monomeric analogue.

Phospholipid monolayers and multilayers represent powerful tools for probing structure–activity relationships of biomembranes.[4-6] Recently, polymeric analogues, having controllable

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