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Magnetic Field Effects on the $Mn(5NO_2SMDPT)$-Catalyzed Oxidation of 2,6-Di-*tert*-butylphenol: ^{2}H and ^{17}O Magnetic Isotope Effects

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The effect of a magnetic field between 0 and 70 kG on the rate of catalytic oxidation of 2,6-di-*tert*-butylphenol (DTBP) to form 2,2′,6,6′-tetra-*tert*-butyldiphenoquinone (DPQ) by [bis(3-((5-nitrosalicylidene)amino)propyl)methylaminato]manganese(II) ($Mn(5NO_2SMDPT)$) in the presence of O_2 is reported. No kinetic ^{2}H isotope effect is observed with DTBP-*O-d*, and DTBP-*4,O-d*$_2$ exhibits mass and magnetic kinetic isotope effects of 1.46 and 1.23, respectively. No ^{17}O kinetic isotope effect is observed for isotopically enriched O_2. These results are compared to the rate of oxidation of DTBP by $Pb(OAc)_4$, which is not affected by a magnetic field between 0 and 70 kG. The $Pb(OAc)_4$ oxidation of DTBP-*4,O-d*$_2$ exhibits a ^{2}H kinetic isotope effect of 1.28. The rate of oxidation of the proposed intermediate 4,4′-dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (TTBBP) by $Mn(5NO_2SMDPT)$ or $Pb(OAc)_4$ gives a maximum rate relative to zero magnetic field of 1.09 ± 0.06 or 1.02 ± 0.07, respectively. These results are discussed in terms of a proposed mechanism.

Introduction

The recent link established between very weak magnetic fields and physiological effects in humans such as an increased incidence of miscarriages[1] and cancer[2] is significant in light of the potential widespread commercialization of superconducting devices.[3] Most investigations of magnetochemical effects involve the photochemical production of radical pairs[4] or electrogenerated chemiluminescence.[5] Typically, these effects are the result of a magnetic field induced perturbation of the recombination rate of radical pairs, which also can occur in thermal radical pair reactions. However, magnetic field effects on thermal chemical reactions continue to be controversial[4,6] although a few magnetochemical studies exist of radical pair reactions known to exhibit chemically induced dynamic nuclear polarization (CIDNP).[7] Since CIDNP signal intensity is related to the rate of intersystem crossing, k(isc), between the singlet and triplet state of the radical pair, the magnetic field is expected to perturb the ratio of singlet and triplet state derived products.[8] This has been observed experimentally in alkyllithium–alkyl halide exchange reactions.[8] The single-electron-transfer (SET) process is dependent on a number of experimental variables such as magnetic field strength, the presence of magnetic isotopes, solvent viscosity, and the nature of the alkyl group. The change in yield of cage and escape products is usually small, between 5 and 15%.[8] This small change in the yield of each product is due to the magnetic field independent rate of the cage escape process.

The effect of an applied magnetic field on the catalytic oxidation of 2,6-di-*tert*-butylphenol (DTBP) to form the corresponding coupled quinone, 2,2′,6,6′-tetra-*tert*-butyldiphenoquinone (DPQ), by [bis(3-((5-nitrosalicylidene)amino)propyl)methylaminato]manganese(II) ($Mn(5NO_2SMDPT)$) complex has been described recently.[9] In contrast to the relatively small magnetic field effect found in stoichiometric reactions, we report a 3-fold change in the rate for the manganese-catalyzed reaction between 0 and 70 kG. Although the magnetic field effect on the intersystem crossing rate between singlet and triplet radical pairs is comparable in the stoichiometric and catalytic processes, the single product formed in this catalytic system involves a step that is magnetic field dependent.[9] This feature facilitates the investigation of the magnetic field effect. Our initial observation has been examined further in order to ascertain if the transition-metal complex is indeed responsible for the magnetic field effect and to derive a better understanding of the catalytic system. The observation of magnetochemical effects in the transition-metal-catalyzed oxidation of an organic substrate suggests an intriguing mechanism for magnetobiological effects.[10]

Experimental Section

Materials. 2,6-Di-*tert*-butylphenol, phenol, bis(3-aminopropyl)methylamine (MeDPT), salicylaldehyde, and $Pb(C_2H_3O_2)_4$ (Aldrich), 5-nitrosalicylaldehyde (Alfa), and $Mn(C_2H_3O_2)_2{\cdot}4H_2O$ (AESAR) were used without further purification. 2,6-Di-*tert*-butyl-4-bromophenol was obtained as a gift from R. S. Drago (University of Florida). Standard gases (air, N_2, O_2, H_2), deuterium gas (99.5%) (Matheson), isotopically enriched O_2 gas (Icon), and deuterated solvents (Aldrich or Norell) were used without purification. The isotopically enriched O_2 was analyzed by Icon: 43.2% ^{16}O, 16.8% ^{17}O, 40.0% ^{18}O. Solvents were purified according to standard literature procedures[11] and stored over molecular sieves.

Instrumentation. Vibrational spectra were obtained on an IBM Instruments FT-85 infrared spectrometer, NMR spectra were collected on either a Bruker AM-300 or a Varian EM-360L spectrometer (^{1}H only), and UV–visible spectra were recorded on an IBM Instruments 9400 spectrometer. Electron-impact mass spectra were run as a service on a double-focusing magnetic sector Finnigan MAT 8200 mass spectrometer via a direct-insertion probe at the MIT Mass Spectrometry Laboratory. Elemental analysis was performed by Schwarzkopf.

Preparation of $Mn(5NO_2SMDPT)$. [Bis(3-((5-nitrosalicylidene)amino)propyl)methylaminato]manganese(II) ($Mn(5NO_2SMDPT)$) was prepared in Schlenkware according to the literature method.[12,13] The orange solid was stored in an inert-atmosphere box. Each batch of $Mn(5NO_2SMDPT)$ was consistent with the literature IR spectrum and elemental analysis.[12,13]

Preparation of 2,6-Di-*tert*-butylphenol-*O-d* (DTBP-*O-d*). 2,6-Di-*tert*-butylphenol deuteriated in the phenolic position was obtained by

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stirring the DTBP-*O-h* with CH_3OD and rotary-evaporating the methanol. The OD stretch is observed at 2680 cm^{-1}, and deuterium substitution based on the relative intensities of the OH and OD stretch is estimated to be 75%.

Preparation of 2,6-Di-*tert*-butylphenol-*4,O-d*$_2$ (DTBP-*4,O-d*$_2$). 2,6-Di-*tert*-butyl-4-bromophenol-*O-d* (3.5×10^{-3} mol), 5% palladium on carbon, and cyclohexene[14] (2% by weight) were added to 25 mL of CH_3OD in a 250-mL Parr pressure bottle (A. H. Thomas Co.) fitted with a pressure gauge and placed in an oil bath. The system was purged with N_2 and charged with 40 psi of D_2. Reactions were run at 30–35 °C with constant stirring for 1–2 weeks, after which no additional pressure drop was observed. The product mixture was filtered through Celite and the solvent removed by rotary evaporation to yield a white solid. ^1H NMR spectra indicated no starting bromophenol (e.g. less than 2%). Elemental analysis indicates that the upper limit of starting material is less than 1.4%. Anal. Calcd for $C_{14}H_{20}OD_2$: C, 81.51; H, 10.94. Found: C, 81.04; H, 10.94; Br, <0.4.

Preparation of C_6H_5OD. Phenol (63 mmol) and sodium methoxide (63 mmol) were dissolved in 100 mL of anhydrous methanol, and the solvent was removed. The sodium phenoxide was shaken with D_2O followed by dropwise addition of a 100-mL CH_2Cl_2 solution containing PCl_3. The resulting white precipitate (NaCl) was removed, the filtrate was extracted with CH_2Cl_2 and dried over $MgSO_4$, and the solvent was stripped. The white solid was charactrized by its OD stretch (2642 cm^{-1}). The relative intensity of the OD/OH stretch indicates the phenol is 70% deuteriated.

Preparation of 4,4′-Dihydroxy-3,3′,5,5′-tetra-*tert*-butylbiphenyl (TTBBP). 2,2′,6,6′-Tetra-*tert*-butyldiphenoquinone (DPQ) (0.39 g) was added to a Parr pressure bottle containing 0.4 g of 5% Pd/C in 40 mL of glacial acetic acid, and the mixture was purged with N_2 and charged with 40 psi of H_2. The mixture was stirred for 12 h, the contents of the Parr bottle were filtered, and the solution was rotary-evaporated. The resulting yellow solid was recrystallized in hexane. The melting point (184–185 °C)[15] and the ^1H NMR spectrum (δ(TMS in $CDCl_3$) 7.3 (m, 4), 5.2 (s, 2), 1.45 (s, 36))[16] were consistent with the literature.

Catalytic Oxidation Studies. In a typical experiment, two fresh stock solutions were prepared, one containing 4.85×10^{-1} M substrate phenol (DTBP or TTBBP) in CH_2Cl_2 and the other containing 8.1×10^{-3} M catalyst ($Mn(5NO_2SMDPT)$) 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. This agitates the solution to ensure that mass transfer of O_2 into the solution is not rate limiting. Dioxygen and substrate phenol are present in sufficient concentration to ensure that the rate of product formation is linear throughout the reaction interval, 23 h unless stated otherwise. Reaction conditions were chosen to prevent product precipitation during the reaction. However, the oxygenated manganese complex is not completely soluble under these conditions.

Zero magnetic field (Earth's field $\simeq$ 0.5 G) measurements were performed by placing the 5-mm NMR tube containing the reactants in an air-driven turbine spinner. The temperature (25.0 ± 1.0 °C) of all kinetic measurements was regulated by a Varian Temperature Controller interfaced to an air-flow system. Laboratory magnetic fields of 0–1.6 T were generated by electromagnets calibrated by a Walker Scientific MG-4D gaussmeter, and the NMR tubes were placed midway between the pole faces of the electromagnet. The 70.05-kG field was obtained from the superconducting magnet of a 300-MHz Bruker NMR spectrometer, and the sample was spun and temperature controlled (25.0 ± 1.0 °C) according to standard procedure.

The $^{17/18}O$-enriched O_2 reactions were performed by use of a modified gas buret system. The isotopically enriched dioxygen was obtained in a 50-mL break-seal flask. This flask was glass-blown to one end of the gas buret, and the reaction mixture was contained in an NMR tube with a constricted opening attached by an O-ring joint to the other end of the gas buret. The NMR tube containing the reaction mixture was placed in liquid nitrogen, and the entire system was evacuated. The isotopically enriched O_2 was admitted into the gas buret and the system allowed to equilibrate. The O_2 condensed into the NMR tube, and the NMR tube was removed from the line by flame-sealing the constriction. The NMR tube was placed in a 25 °C water bath for rapid thermal equilibration and then placed in the air-driven turbine spinner. The amount of gas ($\simeq$3.0 mL) condensed into the NMR tube was measured when the gas buret reached thermal equilibrium.

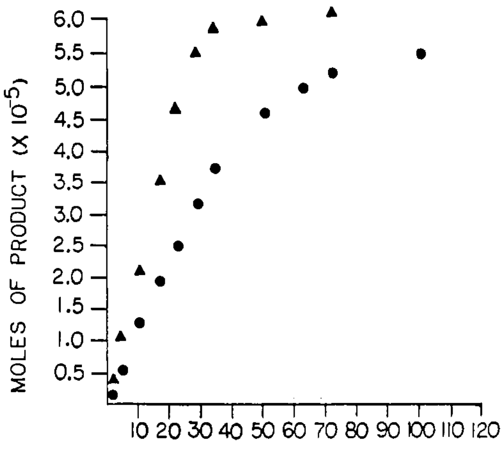

Figure 1. Rate of DPQ formation by $Mn(5NO_2SMDPT)$ at 0.5 (●) and 1390 G (▲).

Table I. Manganese-Catalyzed Oxidation of DTBP at 25 °C: ^2H and ^{17}O Isotope Effects

substrate	*H*, G	10^2k(Mn)	*k*(rel)
DTBP	0	1.69 ± 0.07	
	1390	3.17 ± 0.11	1.88 ± 0.10
DTBP-*O-d*	0	1.78 ± 0.08	
	1390	3.17 ± 0.12	1.78 ± 0.10
DTBP-4,*O-d*$_2$	0	1.16 ± 0.04	
	1390	1.77 ± 0.07	1.53 ± 0.08
DTBP/$^{17}O_2$	0	1.67 ± 0.08	
	1390	3.22 ± 0.11	1.93 ± 0.11
	1390	3.13 ± 0.11	1.87 ± 0.11
TTBBP	0	1.28 ± 0.07	
	1390	1.39 ± 0.08	1.09 ± 0.06

Substrate Oxidation by $Pb(C_2H_3O_4)_4$. A 2.0-mL solution containing DTBP or TTBBP (2.42×10^{-1} M) and $Pb(C_2H_3O_2)_4$ (1.22×10^{-2} M) in benzene was prepared. This solution (0.2 mL) was syringed into a 5-mm NMR tube and allowed to react for 36 h according to the above procedure. The *tert*-butyl ^1H NMR resonances of the product mixture were integrated to determine the extent of the reaction.

Product Analysis. The product yield was obtained by NMR integration of the reaction mixture without product workup. The *tert*-butyl ^1H NMR resonances of DPQ, DTBP, and TTBBP (δ(TMS) 1.33, 1.41, and 1.45, respectively)[16] can be resolved and integrated to indicate the extent of substrate conversion and product identity. The precision required for deuterium isotope studies required the use of a high-resolution NMR spectrometer. The NMR integration of solutions containing DTBP, DPQ, and TTBBP compared with known concentrations of standard solutions within ±0.5%. The NMR integration of the manganese-catalyzed product mixture compared 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 yield was obtained from its absorption spectrum, which follows Beer's law in the range of concentrations observed (diphenoquinone $\epsilon_{425} = 7.64 \times 10^4$ M^{-1} cm^{-1}). Reactions using $^{17}O_2$ were quenched immediately by addition of the reaction tube contents to a silica gel column and chromatographed with CH_2Cl_2 in order to remove the catalyst. The eluted organic material was analyzed via ^1H NMR, IR, and mass spectrometry.

Results

The extent of 2,2′,6,6′-tetra-*tert*-butyldiphenoquinone (DPQ) formation catalyzed by $Mn(5NO_2SMDPT)$ was observed periodically for 100 h at 0.5 and 1390 G. Each point represents a different reaction, where the extent of product formation was measured by ^1H NMR integration of the *tert*-butyl resonances of the substrate and product. The rate of product formation is linear during the initial 30 h of the manganese-catalyzed reaction (Figure 1), and the product yield in this time interval provides a good estimate of the initial rate, $k(Mn) = 1.69 \times 10^{-2}$ M^{-1} s^{-1} at 0.5 G.

The observed rate, *k*(obsd), is calculated from the moles of substrate consumed per second on the basis of ^1H NMR inte-

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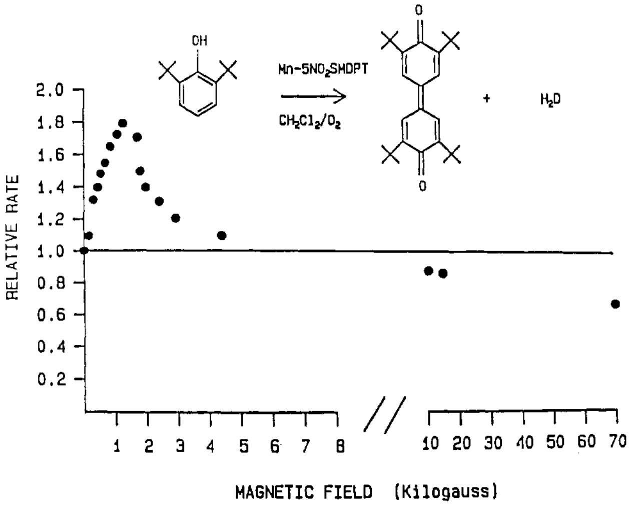


Figure 2. Relative rate of substrate oxidation vs magnetic field strength (*H*).

Table II. $Pb(OAc)_4$ Oxidation of DTBP at 25 °C: Deuterium Isotope Effect

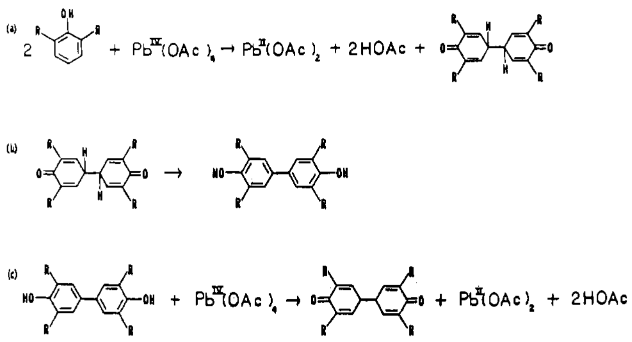
substrate	*H*, G	10^7k(obsd)	*k*(rel)
DTBP	0	2.83 ± 0.12	
	1000	2.75 ± 0.10	0.97 ± 0.05
	4000	2.73 ± 0.11	0.96 ± 0.06
	10000	2.85 ± 0.10	1.01 ± 0.06
	70000	2.80 ± 0.10	0.99 ± 0.05
DTBP-*O-d*	0	2.65 ± 0.11	
	1000	2.76 ± 0.12	1.04 ± 0.06
DTBP-4,*O*-d_2	0	2.17 ± 0.14	
	1000	2.24 ± 0.14	1.03 ± 0.10
TTBBP	0	12.4 ± 1.0	
TTBBP	1000	12.5 ± 0.9	1.01 ± 0.07

gration of the *tert*-butyl resonances of DPQ, TTBBP, and DTBP. The observed rate divided by the moles of manganese present is *k*(Mn). The magnetic field effect on the relative rate of DPQ formation is shown in Figure 2 and in Table I. The vertical axis of Figure 2, *k*(rel), is the ratio of the rate at field *H* divided by the rate at zero magnetic field, which is approximated by Earth's magnetic field of 0.5 gauss. At zero magnetic field strength *k*(rel) is defined as unity. All reported errors correspond to two standard deviations from the mean rate.[18]

The magnetic field effect on the extent of DTBP and TTBBP consumption by the stoichiometric oxidant $Pb(OAc)_4$ is shown in Table II. The first equivalent of $Pb(OAc)_4$ per mole of substrate yields primarily TTBBP along with small amounts of 2,6-di-*tert*-butylquinone and DPQ, and a second equivalent of $Pb(OAc)_4$ converts TTBBP to DPQ.[19] The $Pb(OAc)_4$ oxidation of TTBBP is significantly faster than that of DTBP, while the manganese oxidation of TTBBP is slower than that of DTBP. All errors represent two standard deviations. No magnetic field perturbations of the $Pb(OAc)_4$ reaction rates are observed.

Tables I and II also contain the results of studies with isotopically labeled substrates. The mass and magnetic isotope effect for DTBP deuteriated in the phenolic position (DTBP-*O-d* is negligible for either $Pb(OAc)_4$ or the manganese catalyst. The mass isotope effect observed for the substrate deuteriated at both the phenolic and the para ring position (DTBP-*4,O-d*$_2$) is similar for both $Pb(OAc)_4$ and the manganese catalyst. The mass isotope effect is given by $[k(^1\text{H})/k(^2\text{H})]_0$ (zero magnetic field), which is 1.28 ± 0.08 for $Pb(OAc)_4$ and 1.46 ± 0.06 for the manganese-catalyzed reaction. The maximum magnetic isotope effect is calculated at the field that corresponds to the maximum *k*(rel). The total mass and maximum magnetic isotope effect observed in the manganese reaction is $[k(^1\text{H})/k(^2\text{H})]_{1390} = 1.79 \pm 0.09$. The maximum ^{2}H magnetic isotope effect is $[k(^1\text{H})/k(^2\text{H})]_{1390}/[k(^1\text{H})/k(^2\text{H})]_0 = 1.23 \pm 0.08$. The use of ^{17}O-enriched O_2 gas exhibits no significant change in the rate of the catalyzed reaction, where each rate is the average of at least two runs and the reported error is assumed to be similar to those of comparable experiments that use $^{16}O_2$.

Scheme I



Discussion

The magnetic field dependence of the relative rate, *k*(rel), on *H* is shown in Figure 1 for the manganese-catalyzed oxidation of DTBP to DPQ. Although alternative explanations exist for magnetic field effects, we believe the manganese-catalyzed oxidation is best understood in terms of a radical pair analysis[20] for the following reasons:[21] (1) the reaction involves one-electron redox steps,[22] (2) the observed dependence of *k*(rel) on *H* is of magnitude and profile similar to those of reported magnetic field effects of photogenerated radical pairs derived from substituted ketones,[20] and (3) the magnetic ^{1}H/^{2}H isotope effects (vide supra) are similar to those in radical pair reactions generated photochemically.[23]

Several observations indicate the regeneration of the manganese catalyst is responsible for the magnetic field effect. Because the stoichiometric oxidation of the substrate (DTBP or TTBBP) by one-electron oxidants such as $Pb(C_2H_3O_2)_4$ exhibits no magnetic field effect (Table II), it is evident that phenol coupling or oxidation per se is not associated with a magnetic field effect. Since the magnitude and profile of the observed magnetic field effect on *k*(rel) for Mn(5NO$_2$SMDPT) are similar to but not identical with those for CoSMDPT,[9] the role of the transition metal is implicated. The greater variation in *k*(rel) between 0 and 70 kG for Mn(5NO$_2$SMDPT) than for Co(SMDPT)[9,24] is consistent with the known formulation of the manganese catalyst as a dimer[25] and the cobalt catalyst as a monomer.[26]

The stoichiometric oxidation of DTBP by $Pb(OAc)_4$ is summarized in Scheme I.[15,16,27] When 1 equiv of oxidant is used, TTBBP is the primary product. No ^{2}H isotope is observed in TTBBP formation when the substrate is deuteriated in the phenolic

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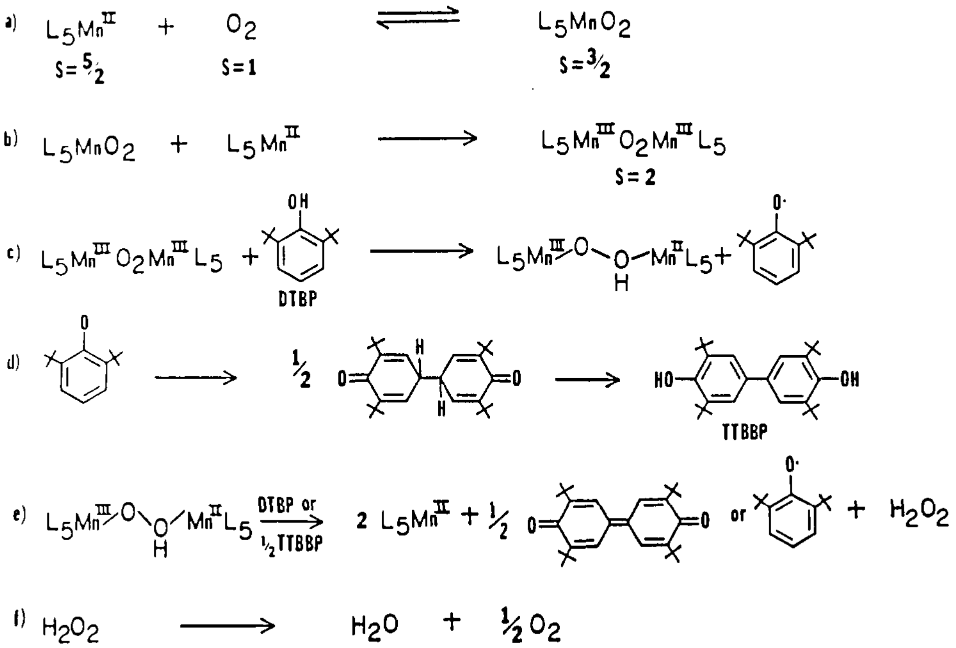
Scheme II



position, and a small mass isotope effect is observed for DTBP-*4,O*-d_2. Furthermore, no magnetic field or magnetic isotope effect is observed for TTBBP formation or the conversion of TTBBP to DPQ by an additional equivalent of Pb(OAc)$_4$.

In contrast to Pb(OAc)$_4$ catalysis, manganese catalysis of DTBP-*4,O*-d_2 exhibits a magnetic isotope effect. The similarity in magnitudes between the mass deuterium isotope effect for Pb(OAc)$_4$ (1.28 ± 0.08) and the catalyst (1.46 ± 0.06) indicates the deuterium mass isotope effect observed in both reactions is the result of the formation of TTBBP. The larger overall ^{2}H isotope effect observed at the maximum k(rel) in the catalytic reaction, $[k(\mathrm{H})/k(\mathrm{D})]_{1390} = 1.79 \pm 0.08$, indicates both the mass and the magnetic ^{2}H isotope effects slow the reaction. Clearly, the ring deuterium atom diminishes the reactivity of DTBP-*4,O*-d_2 to a greater extent than expected for just a mass isotope effect. The magnetic isotope effect is calculated to be 1.23 ± 0.10, which is the total ^{2}H isotope effect divided by the mass isotope effect, $[k(^1\mathrm{H})/k(^2\mathrm{H})]_{1390}/[k(^1\mathrm{H})/k(^2\mathrm{H})]_0$. Since the change in the HFC constant is proportional to the ratio of the ^{1}H and ^{2}H magnetogyric ratios, 6.5, the reduction of the magnetic field effect by ^{2}H is expected.[28] The magnitude of the ^{2}H magnetic isotope effect observed here is comparable to that observed in magnetophotochemical studies of substituted ketones.[23] The para ^{1}H ring hydrogen coupling constant in the 2,6-di-*tert*-butylphenoxy radical is 9.63 G,[29] which is comparable to the ^{1}H coupling found in the radical pairs produced in photolyzed products from ketones.[21]

Scheme II presents a proposed mechanism for the manganese-catalyzed conversion of DTBP to DPQ. The role of O$_2$ in this reaction was investigated to determine if it contributes to the magnetic field effect. In the presence of a protic source and O$_2$, the dimerization rate of Mn(5NO$_2$SMDPT) to form [Mn(5NO$_2$SMDPT)]O$_2$ is rapid[25] compared to the rate of catalysis of DTBP to DPQ. Hence, it is not surprising that the magnetic isotope effect of ^{17}O ($I = {}^5/_2$) enriched O$_2$ ($I = 0$ for ^{16}O and ^{18}O) is less than the experimental error (Table II). This allows steps a and b to be eliminated as the origin of the magnetic field effect. The oxy-bridged dimer, [Mn(5NO$_2$SMDPT)]$_2$O$_2$, has a quintet ground state ($S = 2$).[30] The hydrogen atom abstraction of DTBP by [Mn(5NO$_2$SMDPT)$_2$O$_2$ is expected to generate a phenoxy radical and the bridging hydroxy species suggested in step c. The spin multiplicity of this pair is unknown. However, the absence of an increase in k(rel) corresponding to the energy level crossing of the Zeeman-split quintet-state Q$_{-2}$ sublevel with S_0 at 700 G, the "half-field" transition, indicates either step c is not responsible for the magnetic field effect or the rate of a double-electron-spin-flipping process, Q$_{-2}$–S_0 intersystem crossing, is significantly slower than Q$_{-1}$–S_0 intersystem crossing.[31,32]

The chief differences between the Pb(OAc)$_4$ and the manganese/O$_2$ oxidation reactions are (a) a magnetic field effect observed in the manganese-catalyzed reaction, (b) a magnetic ^{2}H isotope effect associated with the para ring hydrogen only when the manganese catalyst is employed, and (c) the requirement of O$_2$ in the manganese-catalyzed reaction. The absence of a mass or magnetic isotope effect for DTBP-*O-h*/*O-d* indicates that O–H bond cleavage is not the cause of the magnetic field effect and argues against step c of Scheme II. The absence of an observable magnetic field effect in the Pb(OAc)$_4$ oxidation reaction shows that steps a and b of Scheme I, which result in TTBBP, are not perturbed by a magnetic field. For this reason, the same process, step d of Scheme II, is not affected by a magnetic field. The conversion of TTBBP to DPQ, step c of Scheme I, exhibits no magnetic field effect with Pb(OAc)$_4$ and a small (1.09 ± 0.06) magnetic isotope effect with manganese. The rate of TTBBP conversion to DPQ is slower than for the overall conversion of DTBP. This suggests either the catalyst is reduced more efficiently by DTBP than TTBBP in the regeneration step e or DPQ formation is facilitated by the association of the DTBP phenoxy radical with the paramagnetic catalyst throughout the subsequent substrate dimerization and oxidation steps. Therefore, the similarity of the k(rel) versus H profiles for Co(SMDPT)[9] and Mn(5NO$_2$SMDPT) and the absence of any appreciable magnetic field effect in the oxidation either of DTBP by Pb(OAc)$_4$ or of TTBBP by either manganese or Pb(OAc)$_4$ suggests that catalyst regeneration by forming the DTBP radical, step e, is the most likely origin of the magnetic field effect.

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