High yields of expansion products are thus dependent on the preservation of the Al–N bond during the reaction and may therefore be related to the Lewis base strength in the base–alane complex.

In summary, the results presented herein have demonstrated that triethylamine–alane is a useful reagent for the synthesis of a variety of new types of aluminacarboranes, including the only examples of group 13 heterocarboranes in which the heteroatom retains active M–H bonds. The base–alane provides a convenient source of highly reactive Al–H bonds under mild reaction conditions and thus should be a useful expansion reagent for other borane, carborane, and metal cluster systems. Studies aimed at exploring such reactions, as well as examining the reactivity and synthetic utility of the small aluminacarboranes reported herein, are now in progress.

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Registry No. I, 113859-97-5; II, 113859-98-6; III, 113859-99-7; $Et_3N{\cdot}AlH_3$, 12076-08-3; 2,2-$Et_2C_2B_4H_6$, 80583-48-8; $Et_3N{\cdot}BH_3$, 1722-26-5; $Me_3N{\cdot}AlH_3$, 16842-00-5; $Me_3{\cdot}BH_3$, 75-22-9.

Magnetic Field Effects on the Catalytic Oxidation of 2,6-Di-*tert*-butylphenol by CoSMDPT: ^2H and ^{17}O Magnetic Isotope Effects

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Abstract: The effect of a magnetic field between 0 and 70 kG on the catalytic oxidation rate of 2,6-di-*tert*-butylphenol, DTBP, to form 2,6-di-*tert*-butylquinone, BQ, by cobalt(II) bis(3-(salicylideneamino)propyl)methylamine, CoSMDPT, in the presence of O_2 is reported. No kinetic ^2H isotope effect is observed with DTBP-OD, and DTBP-4-d_1-OD exhibits mass and magnetic kinetic isotope effects of 1.25 and 1.22, respectively. In the presence of additive phenol, CoSMDPT catalyzes the formation of 2,2′,6,6′-tetra-*tert*-butyldiphenoquinone, DPQ. The mass and magnetic isotope effects in DPQ formation are negligible for the deuteriation of the phenolic position. DTBP-*4*-d_1-OD in the presence of phenol-OD exhibits kinetic mass and magnetic ^2H isotope effects in DPQ formation of 1.73 and 1.31, respectively. These results are compared to the oxidation rate of DTBP by $Pb(OAc)_4$, which is unaffected by a 0–70-kG magnetic field and has a ^2H kinetic isotope effect of 1.28 for DTBP-*4*-d_1-OD. A significant ^{17}O magnetic isotope effect is observed only for BQ production. The ^{17}O enrichment of BQ given has an overall enrichment factor, $S(f)$ = 1.76, at 9% DTBP conversion. These results are discussed in terms of a proposed mechanism.

Very weak magnetic fields have been linked to human health hazards ranging from an elevated incidence of cancer[1] to miscarriages.[2] This suggests the widespread commercial application of superconducting devices[3] could or might constitute a health risk. However, evidence to link magnetic fields with health hazards remains inconclusive because of the lack of a clear chemical understanding of how magnetic fields can affect biological systems. Without this understanding it is difficult to identify the biological chemistry most likely to exhibit magnetic effects.[4] Most investigations of magnetochemistry have focused on the reactivity of excited-state molecules, which occur in the photochemical production of radical pairs[5] or electrogenerated chemiluminescence.[6] Although the existence of magnetic field effects in chemical reactions that proceed thermally remains controversial,[5,7] a few magnetochemical studies exist of established radical-pair reactions such as alkyl lithium–alkyl halide exchange reactions.[8] The magnetic field effect depends 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.[8] The observation of magnetochemistry in these thermal reactions has generated only limited interest to date. The magnetic field induced change in each product is no greater than 10–15% and is comparable to the reproducibility of these exothermic heterogeneous reactions.[9]

In contrast to the relatively small effects observed in stoichiometric radical-pair reactions, larger magnetochemical effects were observed in catalytic reactions that produce a single product. In a recent study we describe a magnetic field induced threefold change in the rate of the transition-metal-catalyzed O_2 oxidation of 2,6-di-*tert*-butylphenol, DTBP.[10] We have extended our initial observations on the catalyst cobalt(II) bis(3-(salicylidene-

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amino)propyl)methylamine, CoSMDPT, to elucidate the origin of the magnetic field effect. The complicated nature of catalytic reactions makes identification of the reaction step(s) responsible for the magnetochemistry challenging. The similarity in the observed magnetic field effect between the production of 2,6-di-*tert*-butylquinone, BQ, by CoSMDPT and 2,2′,6,6′-tetra-butyldiphenoquinone, DPQ, by Mn(5-NO_2SMDPT)[10] indicates the transition-metal complex is responsible for the observed magnetochemistry. The magnetic field induced change in the rate of product formation has been interpreted to originate from the catalyst regeneration step.[10] Additional evidence that supports the catalyst regeneration step as magnetically active will be described. However, the observation of a very large ^{17}O magnetic isotope effect in the formation of BQ demonstrates that at least one additional step of the catalytic cycle is susceptible to magnetic field effects.

Experimental Section

Materials. 2,6-Di-*tert*-butylphenol, phenol, (3,3-diaminopropyl)-*N*-methylamine (MeDPT), salicylaldehyde, $Pb(C_2H_3O_2)_4$ (Aldrich), 5-nitrosalicylaldehyde (Alfa), and $Co(C_2H_3O_2)_2{\cdot}4H_2O$ (Mallinckrodt) 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 deuteriated 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).[11] by mass spectrometry (17.85% (32), 14.24% (33), 37.19% (34), 13.78% (35), 16.94% (36)), and at the MIT Mass Spectroscopy Laboratory (18.70% (32), 14.75% (33), 35.15% (34), 13.85% (35), 17.45% (36)). Solvents were purified according to standard procedure[12] 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 (^1H 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 Schwartzkopf.

Preparation of CoSMDPT. CoSMDPT was prepared according to published procedures, and the batches of the solid characterized by elemental analysis were consistent with literature values.[13]

Preparation of 2,6-Di-*tert*-butylphenol-OD. Deuteriated 2,6-di-*tert*-butylphenol was obtained by stirring the DTBP-OH with CH_3OD and rotary evaporating the methanol. The OD stretch is observed at 2680 cm^{-1}, and deuterium substitution is estimated to be 75%.

Preparation of 2,6-Di(*tert*-butyl-4-d_1)phenol-OD. 2,6-Di-*tert*-butyl-4-bromophenol-OD (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 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 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 was removed, and the filtrate was extracted by CH_2Cl_2, dried with $MgSO_4$, and solvent stripped. The white solid was characterized 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 solution was purged with N_2 and charged with 40 psi of H_2. The mixture was stirred for 12 h after which the contents of the Parr bottle were filtered through Celite 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 data (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 in CH_2Cl_2 and the other containing the catalyst CoSMDPT (8.1×10^{-3} M) 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 concentrations to ensure that the rate of product formation is linear throughout the reaction interval, 36 h unless stated otherwise. Reaction conditions were chosen to prevent product precipitation during the reaction. Reactions using phenol additive were identical with those above, except a 5:1 excess of phenol to DTBP was contained in the DTBP stock solution.

Zero magnetic field (earth's field $\simeq$0.5 G) measurements were performed by placement of the 5-mm NMR tube containing the reactions in an air-driven turbine spinner. The temperature (25.0 ± 1.0 °C) 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 where the sample can be spun and temperature-controlled.

The $^{17}O^{18}O$-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.

The reagent gas was collected for analysis by mass spectroscopy in the following manner. After the reaction, the remaining gas was collected as follows. The NMR tube was glass-blown onto a tube having a break-seal on one end and an O-ring joint attached to a gas-collection bulb fitted with two Teflon airtight valves with O-ring joints. The gas bulb is evacuated and cooled by liquid N_2, and the reaction gas is condensed into the gas bulb after breaking the break-seal.

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) was added to benzene. This solution (0.2 mL) was syringed immediately 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, BQ, and TTBBP (δ (TMS) 1.33, 1.41, 1.28, and 1.45, respectively)[16,17] 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 cobalt-catalyzed product mixture compares favorably (±5%) to an alternative

(11) The value of total isotope content for ^{16}O and ^{18}O in O_2 is approximately ±1%. By use of simultaneous equations the amount of $^{17}O/^{17}O$ and $^{16}O/^{18}O$ can be calculated. This shows the Icon analysis has an absolute error of ±1% in $^{16}O^{18}O$ content when the ^{17}O content is assumed to be correct. The $^{16}O/^{18}O$ content can be recalculated as 42.2 (1.1) and 41.0 (1.1)% for ^{16}O and ^{18}O, respectively. The MIT MS analysis indicates an ^{16}O content of 42.4 (5)% and an ^{18}O content of 40.7 (5)%. The amount of $^{17}O_2$ is between 2.5 and 2.8%, and the total ^{17}O present is 16.8 (3)%. The composition calculated for *m/e* 34 is near the statistical value for $^{17}O/^{17}O$ of 2.8%, which is confirmed by the mass spectrum of BQ formed at zero magnetic field.

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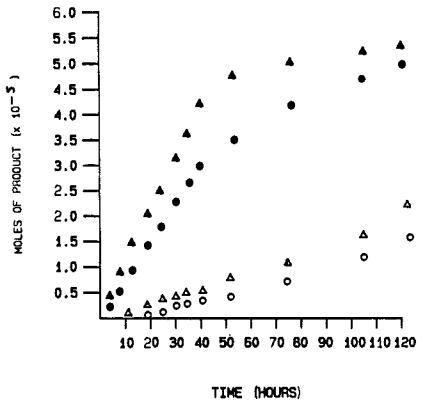

Figure 1. Rate of CoSMDPT-catalyzed formation of BQ at 0.5 (●) and 1000 (▲) G and DPQ formation at 0.5 (○) and 1000 (△) G.

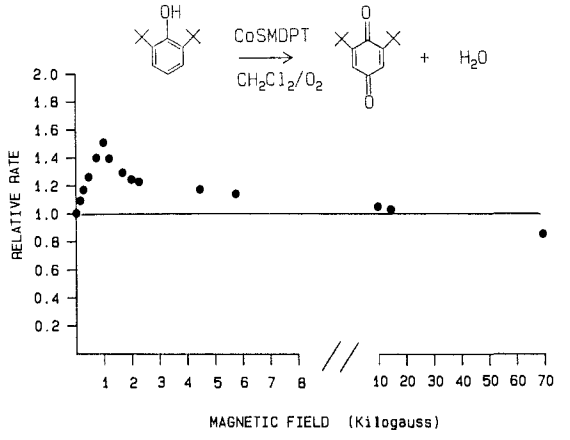

Figure 2. Relative rate of BQ formation vs magnetic field strength (H).

Table I. CoSMDPT-Catalyzed Oxidation of DTBP (Deuterium Isotope Effect)

substrate	H, G	k(Co) × 10^2	k(rel)
	0	1.19 ± 0.05	
DTBP	1000	1.74 ± 0.07	1.46 ± 0.08
	70000	0.99 ± 0.06	0.83 ± 0.04
	0	1.15 ± 0.07	
DTBP-OD	1000	1.71 ± 0.08	1.49 ± 0.11
	0	0.95 ± 0.05	
DTBP-*4*-d_1-OD	1000	1.14 ± 0.08	1.20 ± 0.11
	0	1.26 ± 0.06	
DTBP + phenol	1000	1.85 ± 0.09	1.47 ± 0.10
	0	0.73 ± 0.08	
DTBP-*4*-d_1-OD + phenol	1000	1.01 ± 0.08	1.12 ± 0.15

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 is obtained from its absorption spectrum, which follows Beer's law in the range of concentrations observed (quinone, ϵ_{315} 6.58 × 10^2 M^{-1} cm^{-1}; diphenoquinone, ϵ_{425} 7.64 × 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 2,6-di-*tert*-butylquinone, BQ, formation catalyzed by CoSMDPT was observed periodically until 120 h. Each point in Figure 1 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 41 h of the cobalt-catalyzed reactions (Figure 1), and the product yield in this time interval provides a good estimate of the initial rate; k(Co) = 1.19 × 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 based on the NMR integration

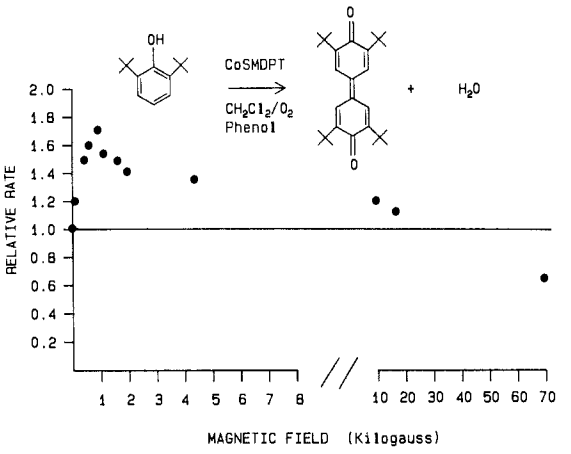

Figure 3. Relative rate of DPQ formation vs magnetic field strength (H).

Table II. $Pb(OAc)_4$ Oxidation of DTBP (Deuterium Isotope Effect)

substrate	H, G	k(obsd) × 10^7	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-OD	0	2.65 ± 0.11	
	1000	2.76 ± 0.12	1.04 ± 0.06
DTBP-*4*-d_1-OD	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

Table III. CoSMDPT-Catalyzed Oxidation of DTBP (^{17}O Isotope Effect)

DTBP convn	H, G	k(Co) × 10^2	k(rel)	% ^{17}O in BQ	S
31.0	0	1.30 ± 0.10		17.5	1.05
62.5	1000	2.63 ± 0.09	2.02 ± 0.17	22.5	1.27
42.8	1000	2.70 ± 0.12	2.08 ± 0.18		
26.3	1000	3.76 ± 0.10	2.89 ± 0.23	26.3	1.76
9.0	1000	4.54 ± 0.13	3.49 ± 0.27	27.5	1.89
9.0	70000	1.14 ± 0.08	0.88 ± 0.09		

of the *tert*-butyl resonances of BQ or DPQ, TTBBP, and DTBP. The observed rate divided by the moles of cobalt present is k(Co). The magnetic field effects on the relative rates of BQ (Figure 2) and DPQ (Figure 3) formation are listed in Table I. The vertical axis of Figures 2 and 3, k(rel), is the ratio of the rate at field H divided by the rate at zero magnetic field, which is approximated by the Earth's magnetic field of 0.5 G. At zero magnetic field strength, k(rel) is defined as unity. All reported errors correspond to 2 standard deviations from the mean k(obsd).[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 equiv of $Pb(OAc)_4$/mol of substrate yields primarily TTBBP along with small amounts of 2,6-di-*tert*-butylquinone and DPQ, and a second 1 equiv 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 2 standard deviations. No magnetic field perturbation of the reaction rate is observed.

Tables I and II also contain the results of studies with isotopically labeled substrates. The mass and magnetic isotope effects for DTBP deuteriated in the phenolic position (DTBP-OD) are negligible for either $Pb(OAc)_4$ or the cobalt catalyst. The small

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mass isotope effect observed for the substrate deuteriated both at the phenolic and in the para ring positions, DTBP-*4*-d_1-OD, is similar in magnitude for both $Pb(OAc)_4$ and the catalyst. The $[k(H)/k(D)]_0$ (zero magnetic field) is 1.28 ± 0.08 for $Pb(OAc)_4$ and 1.25 ± 0.08 for the cobalt-catalyzed reaction. The maximum magnetic isotope effect is calculated at the field that corresponds to the maximum k(rel). The total mass and magnetic isotope effect observed in the cobalt reaction is $[k(H)/k(D)]_{1000} = 1.53 \pm 0.12$. The maximum ^2H magnetic isotope effect is $[k(^1H)/k(^2H)]_{1000}/[k(^1H)/k(^2H)]_0 = 1.22 \pm 0.12$.

The rates obtained for ^{17}O-enriched O_2 oxidant in the catalysis of DTBP to BQ by CoSMDPT are summarized in Table III. Each rate corresponds to the average of at least two runs, and the reported error is assumed to be similar to comparable experiments that use $^{16}O_2$. The rates are calculated by integration of the ^1H NMR spectrum as described above. The intensities of the mass spectra were used to determine the extent of isotopic enrichment of BQ and are accurate to ±0.5%. The overall ^{17}O-enrichment factor,[20] $S(f)$, at the fractional conversion, f, is given by eq 1, where $^{17}O(f)/^{16}O^{18}O(f)$ is the ratio of the concentration

$$S(f) = [^{17}O(f)/^{16}O^{18}O(f)]/[^{17}O(0)/^{16}O^{18}O(0)] \quad (1)$$

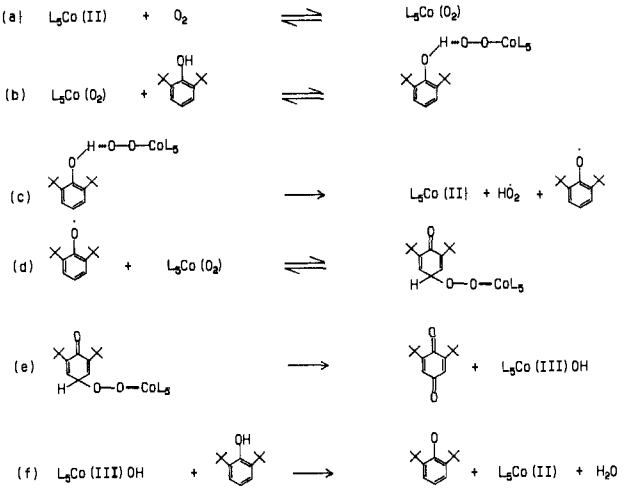
of ^{17}O-enriched BQ to the sum of $^{16}O^{18}O$-containing BQ to the initial concentration of ^{17}O in O_2 divided by the sum $^{16}O^{18}O$ containing O_2 in the reagent gas. The k(rel) values are a measure of effect of the ^{17}O magnetic isotope effect. As can be seen, there is a very large acceleration in BQ production at 1000 G. The initial O_2 to substrate ratio is 2.75 to 1, and the amount of O_2 containing an ^{17}O isotope is about 30%. At high substrate conversion, the ^{17}O-containing O_2 is nearly exhausted. To ensure the reaction products were measured under conditions where ^{17}O-containing O_2 was present in excess, the rate of BQ production was measured at low substrate conversions.

Discussion

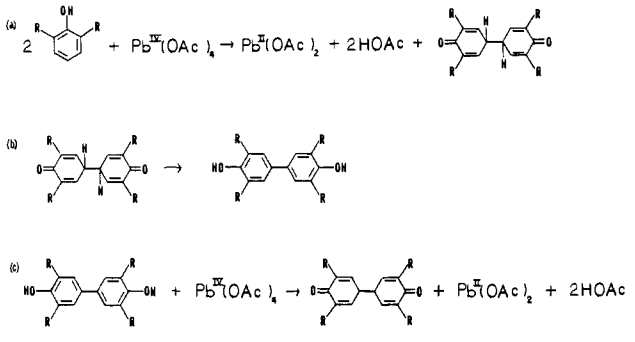
A description of the physical principles responsible for magnetochemistry is the subject of several excellent reviews.[21] Although alternative mechanisms exist to explain magnetochemical effects,[5,22] we believe the cobalt-catalyzed oxidation of DTBP is best understood in terms of a radical-pair analysis. First, the reaction involves one-electron redox steps that form radical species,[23] the observed dependence of k(rel) on H has the same magnitude and profile as reported magnetic field effects of photogenerated radical pairs,[22] and the magnetic $^1H/^2H$ isotope effect (vide supra) is similar to ^2H isotope effects observed in photochemically generated radical-pair reactions.[24]

Several observations implicate the reduction of the cobalt catalyst as the step responsible for the magnetic field effect. First, in sharp contrast to the large magnetic field effect on the rate of oxidation of DTBP by CoSMDPT (shown in Figures 2 and 3), the one-electron oxidation by $Pb(OAc)_4$ of DTBP to TTBBP and TTBBP to DPQ exhibits no magnetic field effect (Table I). On the basis of these observations, it is clear that phenol oxidation or coupling per se is not associated with a magnetic field effect.

Scheme I. Proposed Mechanism of DTBP Oxidation by CoSMDPT



Scheme II. Proposed Mechanism of DTBP Oxidation by $Pb(OAc)_4$



The $Mn(5\text{-}NO_2SMDPT)$[10] catalyst exists as a dimer in solution[25] and exhibits a larger magnetic field effect than monomeric Co(SMDPT), which is consistently a larger separation distance in the radical pair.[21,26]

In a previous communication the CoSMDPT-catalyzed ($S = {}^3/_2$) formation of BQ from DTBP was analyzed in terms of an often proposed mechanism shown in Scheme I. On the basis of an analysis of this mechanism, step f was deduced as the probable origin of the magnetic field effect for the following reasons. The forward rate constant[27] in step a to form the active catalysts, $CoSMDPT(O_2)$ ($S = {}^1/_2$), is reported to be $k = 3.4 \times 10^3$, more than 10^5 times faster than the overall rate of the substrate oxidation, and a 10 000-G magnetic field imparts only a fraction of a kilocalorie to change the free energy of the dioxygen binding equilibrium and cannot alter the concentration of the catalyst significantly. Step b involves the hydrogen bonding of the substrate to the catalyst,[28] which does not involve a change in spin state and is not the origin of a magnetic field effect. Since the reaction initiation step c exhibits no ^2H mass[23] or magnetic isotope effect with DTBP-OD (Table I), it does not contribute to the magnetic field effect.

Conclusive evidence that a step other than d and e is responsible for the observed magnetochemistry is provided by the following experiment. Unsubstituted phenol, C_6H_5OH, is not oxidized by the cobalt–dioxygen catalyst. When a 5/1 ratio of C_6H_5OH to DTBP is used, the competitive hydrogen bonding by C_6H_5OH to the cobalt–dioxygen catalyst prevents the attack by the catalyst on the phenoxy radical required to form BQ.[23] Under these

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(26) As the radical-pair separation distance increases, the singlet–triplet energy gap decreases. This leads to more efficient electron–nuclear hyperfine coupling of the singlet and triplet states, which results in a larger range in k(rel) values versus H.

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conditions the only product is the coupled quinone, DPQ. Although steps d and e are shut off, preventing the formation of BQ, the magnetic field effect for DPQ formation is nearly identical with that for BQ formation when no phenol additive is present (Figures 2 and 3). This is an intriguing result since either step d or e singly or collectively can be considered rate limiting.[23] This indicates the magnetic field affects a process that perturbs the phenoxy radical concentration, which is assumed in the kinetic analysis to have a steady-state concentration.[23] Hence, it can be deduced that the catalyst regeneration step (f), where $Co^{III}SMDPT(OH)$ ($S = 0$) is reduced by the substrate to form phenoxy radicals, is magnetic field dependent. Any process that alters the concentration of the active catalyst (steps a and f) or the phenoxy radical concentration (steps c and f) will affect the reaction rate. The elimination of steps a and c as being responsible for the observed magnetochemistry vide supra implicates step f as magnetically active. This presents an unusual opportunity to study the effect of a reaction step that is not accessible to conventional kinetic and spectroscopic investigations.

The observation of a deuterium isotope effect on the stoichiometric oxidation of DTBP-*4*-d_1-OD by $Pb(OAc)_4$ provides important mechanistic information. The accepted mechanism[19] for the conversion of a 2,6-dialkylphenol to the corresponding coupled phenol by $Pb(OAc)_4$ is summarized in Scheme II. No ^2H isotope effect is observed for the substrate deuteriated in the phenolic position (DTBP-OD). A small mass isotope effect, $[k(^1H)/k(^2H)] = 1.28 \pm 0.08$, is observed in the oxidation of DTBP-*4*-d_1-OD to TTBBP by $Pb(OAc)_4$, and the $[k(^1H)/k(^2H)]$ ratio is independant of magnetic field strength.

In contrast to $Pb(OAc)_4$, the CoSMDPT-catalyzed reaction of DTBP-*4*-d_1-OD exhibits a magnetic isotope effect. The similarity in magnitude between the mass deuterium isotope effect for $Pb(OAc)_4$ and the catalyst, $[k(H)/k(D)]_0 = 1.25 \pm 0.08$ at $H = 0$, indicates the deuterium mass isotope effect observed in the catalytic reaction is probably due to a similar process that results in TTBBP formation. The $[k(H)/k(D)]_{1000}$ isotope effect in the catalytic reaction is 1.53 ± 0.12, which demonstrates that both a mass and a magnetic field effect contribute to slow the reaction. Clearly, the ring deuterium atom diminishes the reactivity of DTBP-*4*-d_1-OD, but at 1000 G, this is to a greater extent than the ^2H isotope effect at zero field. Hence, the observed kinetic ^2H isotope effect is a result of both mass and magnetic effects, where the total isotope effect is given by $k(\text{total}) = k(\text{mag}) \times k(\text{mass})$. The maximum magnetic isotope effect at 1000 G is $[k(^1H)/k(^2H)]_{1000}/[k(^1H)/k(^2H)]_0 = 1.22 \pm 0.16$ for BQ formation and 1.31 ± 0.20 for DPQ production. Since the change in the ^2H electron–nuclear hyperfine coupling constant is proportional to the ratio of the ^1H and ^2H magnetogyric ratios,[29] 6.5, ^2H labeling of the substrate diminishes the magnetic field effect. The magnitude of the ^2H magnetic isotope effect in this reaction is comparable to magnetophotochemical studies of substituted ketones.[24,30]

^{17}O Isotope Effects. The effect of ^{17}O-enriched O_2 on DTBP oxidation by $CoSMDPT(O_2)$ is observed by measuring the change in the reaction rate and the extent of ^{17}O incorporation into the substrate. As seen in Table III, ^{17}O-enriched O_2 accelerates the rate of BQ formation to an appreciable extent. However, when additive phenol is present, the rate of DPQ formation is essentially unchanged. At least one additional step (d or e) responsible for BQ formation must exhibit a large ^{17}O magnetic isotope effect since it is clear that ^{17}O does not alter the rate of catalyst regeneration, step f.

The role of step d in the efficient incorporation of the ^{17}O isotope into BQ can be understood easily. Single-crystal EPR studies of ^{17}O-labeled cobalt–dioxygen adducts show the adduct has one unpaired electron, which resides exclusively on the O_2 ligand with 60 and 40% of the spin density on the terminal and middle oxygens, respectively.[31,32] The ^{17}O hyperfine coupling can enhance the intersystem crossing rate between triplet and singlet states in a radical pair constituted by the phenoxy radical and $CoSMDPT(O_2)$ to form ^{17}O-enriched metalloperoxide.

Step e consists of the conversion of the metalloperoxide[23,33] ($S = 0$) to the diamagnetic oxidized catalyst and BQ. The cleavage of the metalloperoxide could be the result of magnetic field independent two-electron steps or a possible magnetic field dependent hydrogen atom transfer step. There is no persuasive evidence to support step e as the origin of the large observed ^{17}O isotope effect.

The overall isotope enrichment factor, $S(f)$, is measured by observing the intensities of the mass spectrum of the BQ parent ion peaks. At zero magnetic field $S(f)$ equals 1.05 and is consistent with the small increase in the observed reaction rate from 1.19 ± 0.05 to 1.30 ± 0.10 M^{-1} s^{-1}. Although these changes are within experimental error, the fact that the direction of change is the same for both the mass spectrum and the rate suggests that the magnetic ^{17}O isotope accelerates BQ formation at zero field. This is an anticipated result since ^{17}O electron–nuclear coupling is a zero field effect, which can alter the rate of intersystem crossing in the radical pair by coupling the singlet and triplet states. The maximum ^{17}O magnetic isotope effect is observed at 1000 G. As the extent of substrate conversion increases, $S(f)$ decreases because ^{17}O-enriched O_2 has been consumed more efficiently than O_2 containing only $^{16}O^{18}O$, thereby depleating the remaining O_2 of ^{17}O. At 9% conversion the relative concentration of ^{17}O in the O_2 gas has not been affected appreciably. At this level of substrate conversion $k(\text{rel})$ is 3.49 ± 0.27, indicating the rate of reaction of pure $^{17}O_2$ is at least 1 order of magnitude faster[34] than $^{16}O^{18}O$. The increase in $k(\text{rel})$ corresponds to a similar increase in BQ ^{17}O content, from 16.8% in the O_2 reagent gas to 27.5% ^{17}O in the BQ (an absolute change of 64%). At 70 000 G the rate is slower than the zero field rate because the hyperfine coupling process no longer provides an efficient pathway for intersystem crossing.[21] Since the $^{16}O/^{18}O$ ratio in all BQ samples is the same as the initial $^{16}O/^{18}O$ ratio in the reagent gas, this effect can be ascribed to a magnetic ^{17}O kinetic isotope effect.

The correspondence between $k(\text{rel})$ and the extent of the ^{17}O incorporation into BQ indicates that there is no selective orientation of the O_2 molecule in binding to cobalt. The cobalt–oxygen bond formed in step a involves a spin-pairing interaction between an unpaired electron on cobalt(II) ($S = {}^3/_2$) and dioxygen. If this step resulted in the selective formation of Co–^{17}O–O, the resulting BQ would be depleted in ^{17}O not enriched. Either step a is not altered by a magnetic field or the O_2 ligand of $CoSMDPT(O_2)$ is fluxional.

Conclusions

Several reports of magnetic ^{17}O kinetic isotope effects make an interesting comparison. The composition of ^{17}O in the untrapped O_2 formed from 9,10-diphenylanthracene *endo*-peroxide thermolysis in the presence of a $^1O_2$ trap increases from 36.9% ± 0.1 in zero field to 38.0% ± 0.5 at 500 G;[5] $S(f) = 1.07$. The overall enrichment $S(f)$ of the remaining O_2 gas in the dicyclohexyl peroxidicarbonate initiated autoxidation of ethylbenzene in benzene after 80–90% O_2 uptake is 1.13,[35] and the thermal O_2 oxidation of polypropylene initiated by ^{60}Co radiation has an $S(f)$ value of 1.12 at about 75% conversion.[36] A large ^{17}O isotope effect is

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observed during the photolysis of ^{17}O-labeled ketones, which produce a radical pair that can recombine to form ^{17}O-enriched starting ketone. An absolute enrichment of ^{17}O-labeled recovered starting ketone[37] is as high as 21% (from 34.2% ± 0.5 to 41.5% ± 0.5), corresponding to $S(f) = 1.36$.

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Synthesis, Characterization, and X-ray Structure of the Ruthenium "Picnic-Basket" Porphyrins

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Abstract: The synthesis and characterization of a new class of sterically protected porphyrins, the "picnic-basket" porphyrins, are presented. These tetraarylporphyrins, which were prepared as cytochrome P-450 active-site analogues, bear a rigid superstructure on one face of the porphyrin macrocycle. The cavity defined by the appended superstructure may be readily varied in size, chirality, and functionality. In addition, the synthesis and characterization, including an X-ray structure, of several ruthenium picnic-basket porphyrin carbonyl complexes are reported. The regiochemistry of axial ligation in these ruthenium derivatives has been determined by ^1H NMR spectroscopy.

The relevance of synthetic iron porphyrins as hemoglobin and myoglobin active-site analogues has been amply demonstrated during the past 15 years. Elegant syntheses of sterically protected iron porphyrins that reversibly bind molecular oxygen have been reported. Some examples include the "capped" porphyrins of Baldwin and co-workers,[1] the "bridged" porphyrins of Battersby and associates,[2] the "picket fence"[3] and "pocket"[4] porphyrins of Collman and co-workers, the "basket-handle" porphyrins of Momenteau[5a-c] and associates, the "gyroscope" porphyrins of Rose and co-workers,[5d,e] the "cyclophane" porphyrins of Traylor and associates,[6] and the related but nonporphyrinic "lacunar" complexes of Busch and co-workers.[7] These porphyrins bear peripheral appendages that mimic the apoprotein in (1) controlling axial ligand coordination at the iron center and (2) preventing irreversible oxidative dimerization on interaction with dioxygen. Such model compounds have made possible systematic investigations into structural and mechanistic features of dioxygen transport and storage by hemoglobin and myoglobin.

Synthetic porphyrins have also been used to probe dioxygen activation as exhibited by the cytochrome P-450 enzymes. These ubiquitous hemoprotein monooxygenases bind and convert dioxygen into a powerful oxygenating agent capable of hydroxylating unactivated alkanes, epoxidizing alkenes, and oxygenating heteroatoms.[8] Reductive activation of molecular oxygen by simple manganese porphyrins has been achieved with the use of a variety of reducing agents and activating groups.[9] This chemistry has also been extended to iron porphyrins.[10] However, in the presence of dioxygen simple iron(II) porphyrins are thermodynamically unstable and undergo irreversible oxidation to catalytically inactive μ-oxo dimers.[11] In addition, the high affinities of both Fe(II) and Fe(III) porphyrins for axial ligands results in the formation of catalytically inactive bis-ligand species.[12] For these reasons Tabushi et al. have studied iron picket-fence porphyrin as a cy-

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