manganese X-ray absorption spectroscopy, are presently being employed to further characterize these complexes.

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Registry No. 1-Cl, 85185-72-4; **1**-Br, 85185-73-5; **2**-N_3, 79775-62-5; **2**-OCN, 81602-67-7; $[ClMn^{IV}TPP(^{18}OIPh)]_2{}^{18}O$, 85185-74-6; $ClMn^{III}TPP$, 32195-55-4; $BrMn^{III}TPP$, 55290-32-9; iodosylbenzene, 536-80-1; [^{18}O]iodosylbenzene, 80572-92-5.

Hydrocarbon Functionalization by the (Iodosylbenzene)manganese(IV) Porphyrin Complexes from the (Tetraphenylporphinato)manganese(III)–Iodosylbenzene Catalytic Hydrocarbon Oxidation System. Mechanism and Reaction Chemistry

John A. Smegal and Craig L. Hill*

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. *Received September 23, 1982*

Abstract: The two types of complexes isolated from the reaction of (tetraphenylporphinato)manganese(III) derivatives, $XMn^{III}TPP$, with iodosylbenzene—$[XMn^{IV}TPP(OIPh)]_2O$, **1**, X = Cl^- or Br^-, and $[XMn^{IV}TPP]_2O$, **2**, X = N_3^-—are capable of oxidizing alkane substrates in good yields at room temperature. Several lines of evidence establish the intermediacy of free alkyl radicals in the reactions of **1** and **2** with alkanes. Oxygen exchange with water in both the iodosyl (Mn–O–I) and μ-oxo (Mn–O–Mn) moieties of **1** suggests the formation of oxo manganese porphyrin complexes from these moieties. Hydrogen abstraction from the alkane substrate by an oxo manganese porphyrin intermediate is postulated to be the mechanism for reaction of **1** and **2** with alkanes. Observation of a monomeric manganese(IV) porphyrin intermediate by EPR spectroscopy during the reactions of **1** with alkanes is consistent with the formation of a hydroxymanganese(IV) porphyrin complex resulting from substrate hydrogen abstraction by an oxo intermediate. The formation of RX product from oxidation of RH by **1** has been determined to result from ligand-transfer oxidation of free alkyl radicals by the porphyrin complexes in solution. Through competition reactions and time-dependent product formation studies, ligand-transfer oxidation by $XMn^{III}TPP$ was found to be the major pathway for RX production. Observation of $Mn^{II}TPP$ by EPR spectroscopy during the reactions of **1** with alkanes supports this conclusion. Formation of ROH product may result from ligand-transfer oxidation of free radicals or from the collapse of an intermediate caged radical pair. The mechanism of ROH product formation in the caged radical pair is postulated to be an outer-sphere electron-transfer process due to the expected slow rate of inner-sphere ligand transfer for the high-spin d^3 hydroxymanganese(IV) porphyrin complex. Thus the ability of the substrate radical to undergo electron-transfer oxidation determines the ratio of radicals that undergo cage escape to give free radicals to radicals that undergo oxidation and subsequent formation of alcohol product in the caged species. Studies with tertiary substrates support these conclusions.

Manganese porphyrin complexes have been shown to be versatile synthetic oxidation catalysts for the oxidation of a wide variety of organic substances.[1] One of the most interesting oxidation processes mediated by manganese porphyrin complexes is that of alkane oxidation.[1a-e] The activation of C–H bonds, particularly those of saturated hydrocarbons, presents one of the most challenging problems in the field of homogeneous catalysis. Because of the inertness of the strong covalent C–H bond (bond dissociation energies for saturated hydrocarbons range from 91 kcal for tertiary C–H bonds to 104 kcal for methane C–H bonds), very few systems are capable of reacting with alkanes.[2] In nature, the biological activation of alkane C–H bonds is accomplished by the heme-containing monooxygenases, exemplified by the cytochrome P-450 group of enzymes.[3] The development of synthetic oxidation catalysts which are industrially useful as well as possible insight into the mechanistic features of selective hydrocarbon hydroxylation by the cytochrome P-450 enzymes, make these manganese porphyrin catalyzed oxidation processes a subject of great interest. In order to elucidate the mechanism of alkane activation catalyzed by manganese porphyrins, we have isolated and characterized two types of high-valent complexes from the $XMn^{III}TPP$–iodosylbenzene, X = Cl^-, Br^-, N_3^-, and OCN^-, catalytic alkane oxidation system.[4,5] Both types of complexes are dimeric μ-oxo manganese(IV) species. The complexes isolated from the $XMn^{III}TPP$–iodosylbenzene system for X = Cl^- or Br^-, $[XMn^{IV}TPP(OIPh)]_2O$, are distinct from those complexes isolated when X = N_3^- or OCN^-, $[XMn^{IV}TPP]_2O$, in that they contain two additional two-electron oxidizing equivalents in the form of

* Address correspondence to Craig L. Hill, Department of Chemistry, Emory University, Atlanta, Georgia 30322.

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(5) Abbreviation: TPP = *meso*-tetraphenylporphinato dianion ligand.

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iodosyl (Mn–O–I) units. Both types of complexes are capable of oxidizing alkanes in good yields. In this, the third paper in a series of papers regarding alkane activation by the $XMn^{III}TPP$–iodosylbenzene system, we present the reaction chemistry and detailed mechanism of alkane oxidation by these complexes.

Experimental Section

Instrumentation. Visible spectra were recorded on a Cary Model 118 spectrometer. X-band EPR spectra were recorded on a Varian Model E-109 spectrometer with the probe thermostated at 8 K. Gas chromatographic analyses were performed on a Hewlett-Packard Model 5710A gas chromatograph coupled with a Hewlett-Packard Model 3390A reporting integrator. Nitrogen was used as the carrier gas with FID detection. GC columns used for analyses were 0.1% SP-1000 on Carbopak (Supelco, Inc.), 3% FFAP (Analabs) on Chromosorb 103 (Johns-Manville), and a 12-m OV-101 fused silica capillary column (Hewlett-Packard). By variation of the carrier gas flow and column temperature, separation of various components was achieved. The identity of the products was verified by coinjection with authentic samples and in some cases by GC/MS.

Materials. The solvents bromobenzene, chlorobenzene, benzene, *tert*-butylbenzene, and dichloromethane were purified before use by methods described previously.[4a] Cyclohexane was obtained from Burdick and Jackson and was used without further purification. Cyclohexene (Aldrich) was passed over alumina before use. Isobutane (99.5%) was obtained from Matheson Gas Products and was used without further purification. 2,3-Dimethylbutane (Aldrich) was treated with concentrated sulfuric acid and distilled from P_2O_5 before use. 2,2-Diphenyl-1-picrylhydrazyl was obtained from Aldrich. The (iodosylbenzene)-manganese porphyrin complexes **1** and $[N_3Mn^{IV}TPP]_2O$, **2**, were prepared as previously described as were the $XMn^{III}TPP$ complexes.[4]

Reaction of 1 and 2 with the Substrates. All reactions were run anaerobically in Schlenk flasks fitted with Kontes high-vacuum Teflon valves. Solvent and substrate were degassed through several freeze-thaw cycles and then vacuum-transferred into the reaction flask containing the manganese porphyrin reactant. Substrate was always present in at least tenfold excess. Reactions were run at ambient temperature, and completion of the reaction was indicated by disappearance of the brown color of the oxidized porphyrins and formation of the green color of $XMn^{III}TPP$. Reaction times varied from about 1 h for the iodosylbenzene complexes to greater than 24 h for the $[N_3Mn^{IV}TPP]_2O$ complex.

In a typical reaction, 1 mL of cyclohexane and 2 mL of dichloromethane were degassed through three freeze–thaw cycles and vacuum transferred into a Schlenk flask containing (20 mg, 1.07×10^{-5} mol) of **1-Cl**. After ca. 2 h, the solvent, substrate, and products were vacuum transferred away from the $XMn^{III}TPP$ product into a flask and an internal standard was added. Product yields were determined by GLC analysis. For analyses involving high boiling products, the porphyrin reaction solution was submitted directly to GLC analysis. For those substrate systems in which vacuum transfer techniques were used, control experiments with authentic product samples were run to confirm complete transfer of products in the vacuum-transfer process. Isobutane experiments were run by condensing ca. 2 mL of isobutane into a flask which had been cooled to −30 °C. The reaction solvent was then added and the solution degassed by the usual freeze–thaw process. The solution was then vacuum transferred into the reaction flask as usual.

Reaction of 1-Cl (^{18}O Labeled) with Water. To a solution of 5 mL of acetone containing 0.1 mL of H_2O was added (30 mg, 1.61×10^{-5} mol) of 90% ^{18}O-labeled **1-Cl**.[4b] After 5 min the solution was cooled to −50 °C and the resulting microcrystalline product was collected, washed with heptane, and dried in vacuo.

Results

Alkane Oxidation by 1 and 2. The high-valent manganese porphyrin complexes $[XMn^{IV}TPP(OIPh)]_2O$, **1**, X = Cl^- or Br^-, and $[XMn^{IV}TPP]_2O$, **2**, X = N_3^-, react with alkanes in relatively inert solvents at 25 °C to give good yields of functionalized products. The yields of the oxidation products obtained from the reaction of **1** or **2** with primary, secondary, and tertiary alkanes are given in Table I. In addition to the oxidation products, the reaction of the iodosylbenzene complexes, **1**, with alkanes produces 2 equiv of iodobenzene. The oxidizing equivalents not accounted for by substrate oxidation have probably gone toward oxidation of the porphyrin ring and solvent. Control experiments show that when PhIO is substituted for the complexes **1** and **2**, no alkane activation is observed. The reaction of the iodosylbenzene complexes, **1**, with alkanes is very fast at room temperature, with complete reaction requiring about 1 h, whereas reaction of the azide complex, **2**, is relatively slow, with complete reaction requiring more than 24 h. The tertiary to primary selectivity ratio of the isobutane oxidation by **1** is 200:1. Control experiments have determined that isomerization of the isobutane oxidation products does not occur under the reaction conditions.

Table I. Product Yields[a] from the Oxidation of Alkanes by 1 and 2

A. Oxidation of Cyclohexane

	% yield				
reactant	RX	ROH	RO[b]	RR	PhI[c]
1-Cl	24[d]	16	5	1	83
1-Br	27[e]	5	5	1	80
2	30[g]	5	3	1	

B. Oxidation of Isobutane

	% yield				
reactant	*t*-BuOH	*t*-BuX	*iso*-BuX	*iso*-BuOH	PhI[c]
1-Cl	16	19[d]	2[d]	*f*	85
1-Br	11	13[e]	2[e]	*f*	83

C. Oxidation of *tert*-Butylbenzene[h]

	% yield[i]				
reactant	ROH	RX	R'OH	R'X	PhI
1-Cl	2	16	1	1	60

[a] Based on three oxidizing equivalents for 1 and one oxidizing equivalent for **2**. All reactions were run anaerobically at 25 °C with substrate present in excess. PhCl was used as solvent for reactions of 1 and CH_2Cl_2 for 2. Yields represent averages of several reactions. [b] Cyclohexanone. [c] Yield based on 2 PhI/dimer. [d] X = Cl. [e] X = Br. [f] Below detectable limit. [g] X = N_3. [h] *tert*-butylbenzene was used as both solvent and substrate. [i] R = neophyl moiety and R' = benzyldimethylcarbinyl moiety.

Alkane Oxidation by 1 in the Presence of DPPH. The addition of 1 equiv of the radical scavenger 2,2-diphenyl-1-picrylhydrazyl (DPPH) to the reactions of **1–Cl** with primary, secondary, and tertiary substrates resulted in the complete suppression of halogenated product. Halogenated product was not detected for any of the substrate oxidations although some alcohol product was produced in each case. The following yields of alcohol product were observed for 2,3-dimethylbutane, cyclohexane, and *tert*-butylbenzene oxidation by **1-Cl** in the presence of DPPH: 2,3-dimethyl-2-butanol, 5%; cyclohexanol, 4%; neophyl alcohol, <1%. The compound DPPH was selected from the various compounds known to scavenge free radicals because it is one of the most stable of the scavengers to oxidation. Direct comparison, however, of yields obtained from reactions of **1-Cl** in the presence of DPPH with those obtained in the absence of DPPH are misleading due to possible reaction of **1-Cl** with the radical scavenger, resulting in a lower overall yield of product. Comparison of relative product yields from the same reaction, as was done in this section, is not subject to this problem.

Alkane Oxidation by 1 in the Presence of Added $XMn^{III}TPP$. The addition of $X'Mn^{III}TPP$ complexes with axial ligands different than those of the reactant complex **1** to the reaction of **1** with alkanes results in products derived from the added $X'Mn^{III}TPP$ (Table II). The products produced from the added $X'Mn^{III}TPP$ are formed at the expense of those products derived from the reactant complex **1** with the overall yield of products remaining constant. For the oxidation of isobutane by **1** in the presence of added $X'Mn^{III}TPP$, the following features are noteworthy: (1) The yield of alcohol product remains relatively constant, whereas the yield of halogenated product is greatly affected by the presence of the added $X'Mn^{III}TPP$. (2) In all cases, primary alcohol is not observed, although primary halogenated product is always produced.

Time Dependence of 2-Chloro-2,3-dimethylbutane Formation. The time dependence of the formation of 2-chloro-2,3-di-

Table II. Product Yields[a] from the Oxidation of Alkanes by 1 in the Presence of X'Mn^{III}TPP

A. Oxidation of Cyclohexane

reactant	X'Mn^{III}TPP X' =	% yield RX	RX'	ROH	ROH:RX
1-Cl		24[b]		16	
1-Cl	Br	7[b]	25	5	
1-Cl	N_3	7[b]	29	3	
1-Br		27[c]		5	0.2
1-Br	Cl	20[c]	7	5	
1-Br	OH	12[c]	4		0.3

B. Oxidation of Isobutane

reactant	X'Mn^{III}TPP X' =	% yield *t*-BuOH	*t*-BuX	*iso*-BuOH	*iso*-BuX	*t*-BuX'	*iso*-BuX'
1-Cl		16	19[b]	*d*	2		
1-Cl	Cl	14	26[b]	*d*	2		
1-Cl	Br	11	6[b]	*d*	2	18	2
1-Br		11	13[c]	*d*	2		
1-Br	Br	9	12[c]	*d*	2		
1-Br	Cl	10	11[c]	*d*	2	7	

[a] Based on three oxidizing equivalents for 1. All reactions were run anaerobically in all glass vessels at 25 °C with the substrate present in excess. Yields represent an average of several reactions. Chloro- and bromobenzenes were used as solvent. [b] X = Cl. [c] X = Br. [d] Below detectable limit.

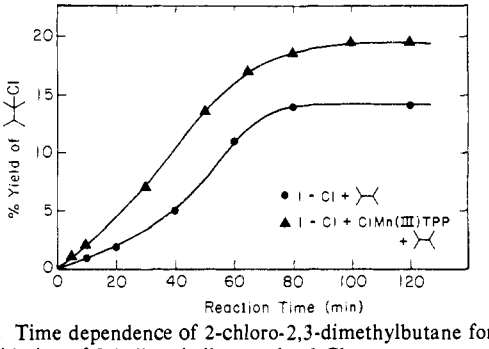

Figure 1. Time dependence of 2-chloro-2,3-dimethylbutane formation in the oxidation of 2,3-dimethylbutane by **1**-Cl.

methylbutane from the reaction of **1-Cl** with 2,3-dimethylbutane with and without added ClMn^{III}TPP is presented in Figure 1. In the absence of added ClMn^{III}TPP, halogenated product is not observed until a reaction time of 10 min, whereas in the presence of added ClMn^{III}TPP, product formation is greatly increased with substantial product detected after only 5 min of reaction time.

Oxidation of Isobutane by the Complex 1-Cl Resulting from Substituted Iodosylbenzenes. The oxidation of isobutane by the (iodosylbenzene)manganese porphyrin complexes formed from substituted iodosylbenzenes produces the product yields listed in Table III. Only the iodosylbenzene complex formed from *p*-methoxyiodosylbenzene affects the product distribution normally obtained for this reaction.

Oxidation of Cyclohexene by 1-Cl and 2. The oxidation of cyclohexene by **1-Cl** produced the following oxidation products: 3-chlorocyclohexene, 32%; 2-cyclohexen-1-ol, 7%; cyclohexene oxide, 31%; 2-cyclohexen-1-one, 1%. Oxidation of cyclohexene by the complex **2**, however, produced almost entirely allylic product: 2-azidocyclohexene, 41%; cyclohexene oxide, 4%. The oxidation products 2-cyclohexen-1-ol and 2-cyclohexen-1-one were present in <1%.

Exchange of Oxygen in 1-Cl with Water. When the 90% ^{18}O-labeled complex **1-Cl** is dissolved in the presence of a small amount of water, then reisolated after a period of 5 min, the IR spectrum shows the return of the μ-oxo (Mn–^{16}O–Mn) absorption at 810 cm^{-1}, as well as the return of the Mn–^{16}O–I absorption at 575 cm^{-1} to its original intensity.[4b] These results indicate that oxygen exchange has occurred in both the Mn–O–Mn and Mn–O–I moieties.

Spectroscopic Monitoring of the Oxidation of Alkanes by 1-Cl. Electronic Spectra. Monitoring the reaction of cyclohexane with **1-Cl** by visible spectroscopy shows a clean conversion of the

Table III. Oxidation of Isobutane by Substituted (Iodosylbenzene)manganese Porphyrin Complexes

[ClMn^{IV}TPP(Y)]$_2$O Y =	% yield[a] *t*-BuOH	*t*-BuCl	*iso*-BuCl	*t*-BuCl: *t*-BuOH
iodosylbenzene	16	19	2	1.2
p-methoxyiodosylbenzene	13	28	2	2.1
2,6-dimethyliodosylbenzene	11	10	1	1.0

[a] Based on three oxidizing equivalents per dimer. All reactions were run anaerobically in all galss vessels at 25 °C with the substrate present in excess. Chlorobenzene was used as the solvent. Yields represent the average of several runs.

reactant **1-Cl** (λ_{max} = 421 nm) to the ClMn^{III}TPP complex (λ_{max} = 476 nm), producing a spectrum with six isosbestic points. The isosbestic behavior displayed here by the (iodosylbenzene)manganese porphyrin complexes is identical with the spectral behavior displayed in the catalytic hydrocarbon activation by XMn^{III}TPP–iodosylbenzene.[1b,c] The position of the Soret band of the XMn^{III}TPP product produced during the reaction is determined by the ligand X in the starting complex **1**, indicating that although the ligand may be bound to the iodine in the reactant complex, it is bound to the metal in the XMn^{III}TPP produced during the reaction.[6]

EPR Spectroscopy. When the reaction of *tert*-butylbenzene with the complex **1-Cl** in chlorobenzene is monitored by EPR spectroscopy, the spectra shown in Figure 2 are obtained. The initial t = 0 spectrum, a in Figure 2, of reactant **1-Cl** shows only two faint signals, one at $g \approx 5$ and one at $g \approx 2$, probably due to traces of monomeric Mn(IV)[7] and μ-oxo Mn(III)Mn(IV) dimer[8] impurities, respectively. The reactant **1-Cl** is EPR silent. Spectrum b produced after a reaction time of 15 min shows an EPR active species with a pronounced six-line hyperfine splitting ($a^{Mn} \approx 75$ G) by the ^{55}Mn ($I = {}^5/_2$) nucleus in the g_z region (~2). This spectrum is indicative of a monomeric Mn(IV) porphyrin species and is of the same type displayed by the monomeric

(6) The frequency of the Soret band for manganese(III) porphyrins is dependent on the axial ligand with the energy order being $F^- > C_2H_3O_2^- > NCO^- > NO_2^- > OH^- \approx Cl^- > N_3^- \approx NCS^- \sim Br^- > I^-$. In strongly coordinating solvents where the axial ligands are displaced by solvent molecules, the frequency of the Soret band is independent of axial ligand. See: Boucher, L. J. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 409–419.

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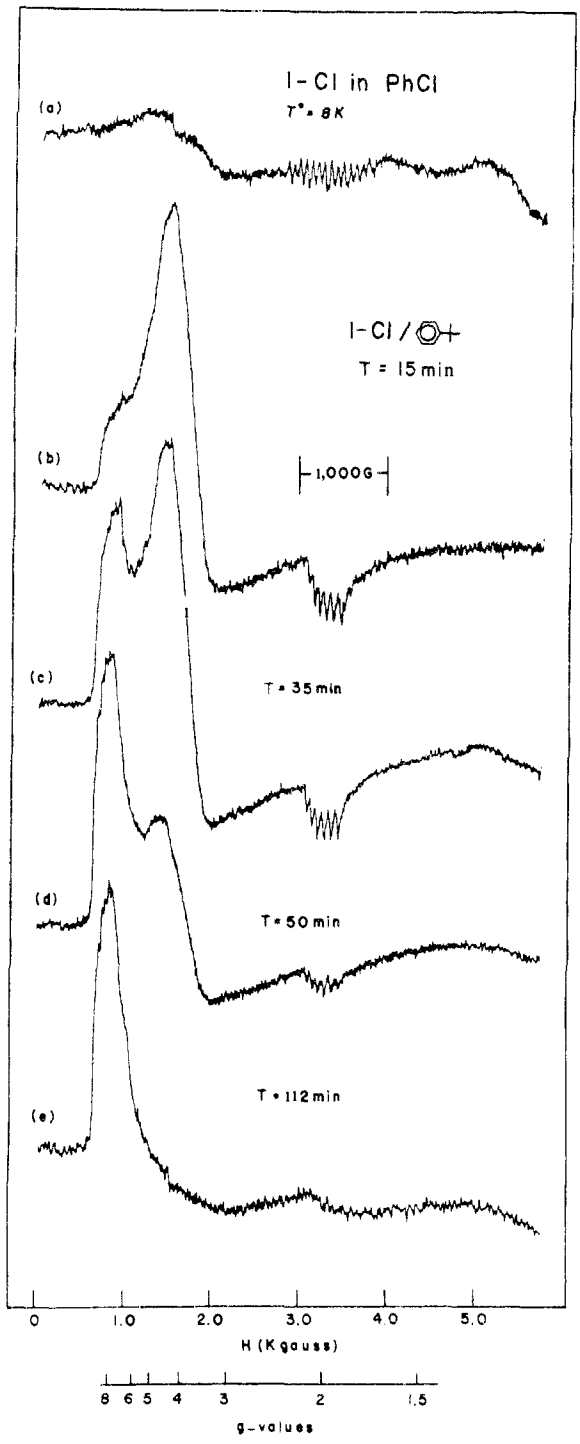

Figure 2. Time dependence of the EPR spectra for the reaction of **1-Cl** with *tert*-butylbenzene: (a) reactant **1-Cl** in the absence of substrate; (b) EPR signal of a monomeric Mn(IV) intermediate after 15-min reaction time at 25 °C; (c) emergence of a Mn(II) signal (35-min reaction time, 25 °C); (d) decrease in Mn(IV) signal with increase in Mn(II) signal (50-min reaction time, 25 °C); (e) EPR signal of Mn(II) (112-min reaction time, 25 °C). All spectra were recorded at 8–10 K. Spectrometer settings: microwave frequency = 9.2 GHz; modulation amplitude, 1 × 10; gain, (2–3.2) × 10^4; power; 2 mW; scan time, 16 min/spectrum.

Mn(IV) complex reported by Sawyer.[7] Recently, a family of EPR active monomeric Mn(IV) porphyrin complexes, $Mn^{IV}TPPX_2$, X = OCH_3,[9] F, Cl, OCN, and N_3,[10] were prepared and characterized. All these complexes are d^3 Mn(IV) neutral porphyrin complexes with $^4A_{2g}$ ground states and display diagnostic $S = {}^3/_2$ EPR spectra, similar to the one observed in spectrum b of Figure 2. The anisotropic spectrum of the Mn(IV) porphyrin complex observed in spectrum b displays a broad resonance at $g_\perp = 4.5$ and a clean six-line hyperfine pattern at $g_\parallel = 2$, indicative of an axially symmetric field that has a large value for the zero field splitting parameter (D) such that $D \gg h\nu$.[11] The large value for D indicates that the species is tetragonally distorted from octahedral symmetry. As the reaction progresses, the Mn(IV) signal is gradually replaced by a new signal at $g \approx 7$. Three lines of evidence establish that this new signal is due to $Mn^{II}TPP$: (1) Authentic $Mn^{II}TPP$ gives the same EPR spectra. (2) Treatment of the reaction solution producing spectrum e in Figure 2 with an oxidizing agent, *N*-bromosuccinimide, eliminates the signal, indicating the formation of the EPR silent Mn(III) porphyrin species. (3) Treatment of the solution with aqueous HCl produces the isotopic ($g \approx 2$) six-hyperfine-line spectrum ($a^{Mn} \approx 90$ G) of $Mn(H_2O)_6^{2+}$ resulting from porphyrin demetalation. Only Mn(II) porphyrins demetalate under these mild conditions.[12] The amount of $Mn^{II}TPP$ present in the reaction can be established by a comparison of its signal with the signal of a known concentration of authentic $Mn^{II}TPP$. In this manner, we can estimate that the Mn(II) complex is present in low concentrations (<1%). This would be expected if the $Mn^{II}TPP$ was in large part oxidized by the other manganese porphyrins in solution. A control experiment indicates that the reactant complex **1-Cl** oxidizes $Mn^{II}TPP$.

Discussion

Alkane Oxidation by 1 and 2. Both types of complexes isolated from the $XMn^{III}TPP$–iodosylbenzene catalytic hydrocarbon functionalization system, $[XMn^{IV}TPP(OIPh)]_2O$, **1**, X = Cl^- or Br^-, and $[XMn^{IV}TPP]_2O$, **2**, for X = N_3^-, react to oxidize alkanes in relatively inert solvents at room temperature (Table I). In the previous paper, it was determined that the iodosylbenzene complexes have two types of oxidizing moieties, one derived from the μ-oxo (Mn–O–Mn) unit and the other from the iodosyl (Mn–O–I) units. The ability of the complex $[N_3Mn^{IV}TPP]_2O$ to activate alkanes indicates that the μ-oxo moiety, a unit which is common to both **1** and **2**, correlates with alkane oxidation. That the iodosyl moieties are also linked to alkane activation is apparent from the yields of oxidized products obtained from the reactions of these complexes with alkanes. These yields indicate that the iodosylbenzene complexes have at least a four-electron alkane oxidizing capability. The oxidation of isobutane by **1** and **2** indicates that these complexes have a relatively high selectivity toward activation of tertiary C–H bonds. The selectivities obtained, however, indicate that oxidation by halogen radical, X·, is not an important pathway in these reactions.

Intermediacy of Free Alkyl Radicals. Several lines of evidence indicate the presence of free alkyl radicals in the alkane activation reactions. The first indication of intermediate free radicals is found in the observation of the radical coupling product dicyclohexyl and the radical addition product cyclohexylbenzene produced when cyclohexane is oxidized by **1** in benzene solvent. Further evidence for free radical intermediates is obtained from the reaction of **1-Cl** and *tert*-butylbenzene (Table I). As shown in Scheme I, a neophyl radical, **4**, formed in the reaction of *tert*-butylbenzene, **3**, with **1-Cl** would undergo some rearrangement to the benzyldimethylcarbinyl radical, **5**, if sufficiently long-lived. The observation of small amounts of rearranged products would, therefore, indicate the presence of intermediate free radicals. If, however, the neophyl carbonium ion is produced in the reaction, quantitative rearrangement via the bridged phenonium ion intermediate, **6**, would result exclusively in benzyldimethylcarbinyl products. The observed product distribution (Table I) indicates the presence of freely diffusing radical intermediates which are long-lived. On the basis of the known rate constant ($k_r = 59\ s^{-1}$) for the neophyl radical rearrangement in nonpolar solvents at 25 °C,[13] the ap-

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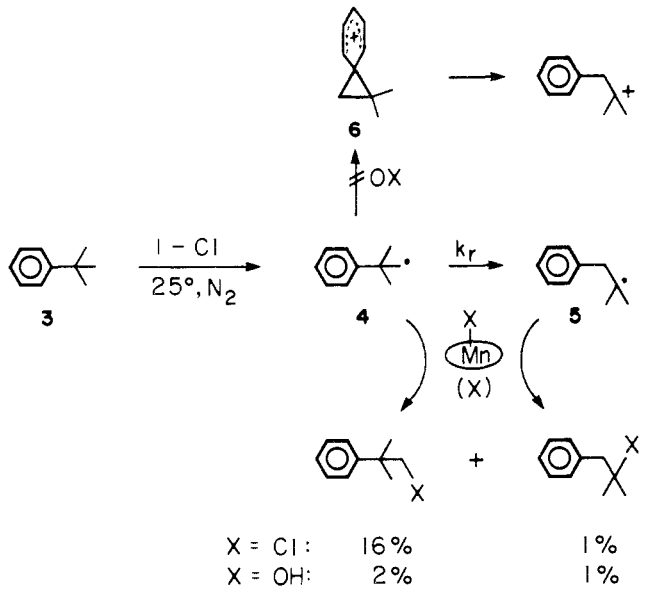
(11) Similar properties of several chromium(III) tris(chelates) have been interpreted in this manner: Singer, L. S. *J. Chem. Phys.* **1955**, *23*, 379–388.
(12) Boucher, L. J. *Coord. Chem. Rev.* **1972**, *7*, 289–329.
(13) Maillard, B.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 1224–1226.

Scheme I

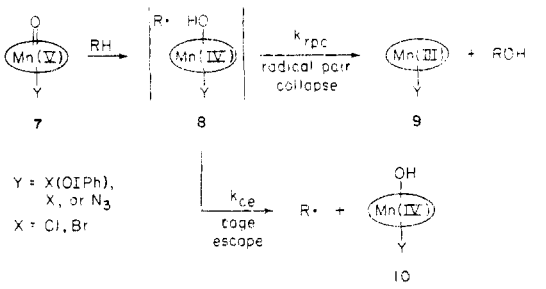


proximate half-live of the free radicals is calculated to be about 2–6 ms.

The last line of evidence for free radical intermediates is obtained from the use of radical traps. The addition of at least 1 equiv of a radical trap should effectively scavenge the relatively long-lived free radicals produced in these reactions, and the products normally resulting from these free alkyl radicals would, therefore, not be observed. The results in Table II show that halogenated product has been completely suppressed, indicating that it is formed exclusively from free alkyl radicals in solution. A small amount of alcohol product is observed in each case, indicating that some of the alcohol product is not produced by long-lived free alkyl radicals. We can conclude, therefore, not only that freely diffusing radicals are produced in the alkane functionalization reactions and that halogenated product is produced exclusively from these radicals but also that some alcohol product formation occurs via a pathway which does not involve long-lived free alkyl radicals.

Description of Activating Species. The presence of free alkyl radicals in the oxidation of alkanes by **1** and **2** suggests an activating species derived from the Mn–O–Mn and Mn–O–I moieties that reacts with alkanes by abstraction of a hydrogen atom. An idea as to the nature of the activating species responsible for the oxidation of alkanes by these complexes is indicated by the result of oxygen exchange with water. This result shows that oxygen exchange occurs in both the Mn–O–Mn and Mn–O–I moieties of the complex **1-Cl**. Oxygen exchange with water has been shown to occur with oxometal complexes such as the reactive oxo(porphyrinato)chromium(V) complex of Groves and Kruper[14] as well as with other oxo transition-metal complexes.[15] The observed exchange of the oxygen in both the Mn–O–Mn and Mn–O–I moieties with water suggests the intermediacy of oxo complexes formed from these units. The incorporation of ^{18}O into the complex $[OCNMn^{IV}TPP]_2{}^{16}O$ with ^{18}O-labeled water was demonstrated in a previous paper.[4a] The water exchange displayed by this complex also suggests the intermediacy of the oxo species. High-valent oxo complexes have been postulated to be the primary species responsible for C–H bond cleavage in the cytochrome P-450 enzymes[3,16] and in the high-valent synthetic metallo-

Scheme II



porphyrin complex of iron which serves as a model for the heme active site of cytochrome P-450.[17]

An alternate mechanism for alkane activation by the iodosyl moiety (Mn–O–I) involves the formation of an iodine-centered radical as the activating species. In this mechanism, an initiation step involving cleavage of the I–X bond or a propagation step in which X· is abstracted by another radical species would produce an iodinanyl radical. Alkane activation by the iodinanyl radical occurs by abstraction of a hydrogen atom from the substrate producing a hydridoiodinane and an alkyl radical. This is analogous to the mechanism postulated by Martin for the halogenation of alkanes by bromo- and chloroarylalkoxyiodinanes.[18] These tricoordinate iodine(III) complexes act as free radical halogenating agents through the intermediacy of cyclic iodinanyl radicals. Iodinanyl radicals have also been proposed in several other iodinane reactions.[19] The iodinanyl activation mechanism as a major pathway for alkane oxidation by the iodosyl moiety (Mn–O–I) is not consistent, however, with olefin oxidation results. These results show that the alkane activating species derived from the μ-oxo (Mn–O–Mn) oxidizing moiety of **2** produces almost entirely allylic product, whereas the iodosylbenzene complex **1-Cl** produces epoxide to about the same degree as allylic product. This suggests that the epoxide formation in the iodosyl complexes is a result of oxidation by the iodosyl moieties. Iodinanyl radicals, however, are known to react with olefins by allylic hydrogen abstraction to yield allylic radicals. Thus, the reaction of cyclohexene with the chloroarylalkoxyiodinane of Martin produced a 95% yield of 3-chlorocyclohexene.[18] If the mechanism of oxidation by the iodosyl moieties of the porphyrin complexes involved iodinanyl radicals as intermediates, only allylic products would be expected for the cyclohexene oxidation by **1-Cl**. These results are consistent with hydrogen atom abstraction occurring primarily at oxygen rather than at the iodine of the iodosyl moiety.

The monitoring of the reaction of alkanes with **1** has indicated the formation of intermediate Mn(IV) monomeric porphyrin complexes during the reaction. A mechanism for the reaction of alkanes with the oxo intermediate that is consistent with this observation is shown in Scheme II. Abstraction of a hydrogen atom from the substrate by an intermediate oxo complex, **7**, would initially form the caged complex, **8**, consisting of the alkyl radical and a hydroxymanganese(IV) intermediate. Recombination of the alkyl radical with the manganese intermediate would produce hydroxylated product and the manganese(III) porphyrin. The alcohol product observed in the reactions of **1** in the presence of DPPH can be accounted for by this pathway. Alternatively, the radical may diffuse out of the solvent cage to produce a free radical and the hydroxymanganese(IV) species, **10**. A hydroxymanganese(IV) species, **10**, would be expected to display an an-

(14) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613–7615.

(15) (a) Murmann, R. K. *J. Am. Chem. Soc.* **1974**, *96*, 7836–7837. (b) Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *Ibid.* **1972**, *94*, 295–296.

(16) (a) Coon, M. J.; Vermilion, J. L.; Vatsis, K. P.; French, J. S.; Dean, W. L.; Haugen, D. A. *ACS Symp. Ser.* **1977**, *No. 44*, 46. (b) Pryor, W. A. "Free Radicals in Biology"; Pryor, W. A., Ed.; Academic Press: New York, 1976; p 1. (c) Groves, J. T.; McClusky, G. A.; White, R. E.; Coon, M. J. *Biochem. Biophys. Res. Commun.* **1978**, *81*, 154–160.

(17) (a) Groves, J. T.; Kruper, W. J.; Nemo, T. E.; Myers, R. S. *J. Mol. Catal.* **1980**, *7*, 169–177. (b) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032–1033. (c) Chang, C. K.; Kuo, M.-S. *Ibid.* **1979**, *101*, 3413–3415.

(18) Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 3060–3065.

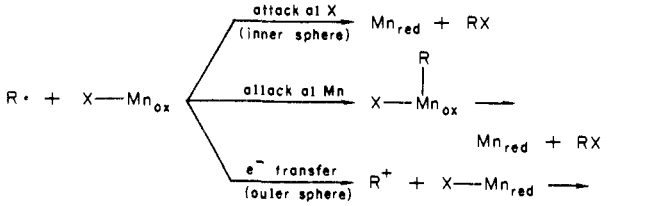
(19) For other examples of iodinanyl radical oxidations see: (a) Banks, D. F.; Huyser, E. S.; Kleinburg, J. *J. Org. Chem.* **1964**, *29*, 3692–3693. (b) Tanner, D. D.; Van Bostelen, P. B. *Ibid.* **1967**, *32*, 1517–1521. (c) Tanner, D. D.; Gidley, G. C. *Ibid.* **1968**, *33*, 38–43. (d) Tanner, D. D.; Gidley, G. C. *J. Am. Chem. Soc.* **1968**, *90*, 808–809. (e) Heusler, K.; Kalvoda, J. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 525–538. (f) Tanner, D. D.; Gidley, G. C. *Can. J. Chem.* **1968**, *46*, 3537–3544.

isotropic spectrum similar to that observed in the reaction of **1-Cl** with *tert*-butylbenzene (Figure 2).

Because of the uncertainty in the structure of the iodosylbenzene complexes and the location of the ligands X,[4b] whether iodobenzene constitutes an integral part of the oxo intermediate formed from the iodosyl unit is also uncertain. The effect of the iodobenzene in determining product distribution is indicated from Mn^{IV}—O·, reaction of isobutane with the (iodosylbenzene)manganese(IV) porphyrin complex formed from *p*-methoxyiodosylbenzene[20] (Table III). Product analysis shows that the ratio of *tert*-butyl chloride to *tert*-butyl alcohol goes from ca. 1:1 for the unsubstituted iodosylbenzene complex to ca. 2:1 for the *p*-methoxyiodosylbenzene complex. This result shows that the iodobenzene is capable of influencing product distribution in these reactions, although as Table III shows, this is not always the case.

The formulation as Mn(V) for the oxo complexes in Scheme II is a formal oxidation state and, as such, is a convention used for convenience. A formulation having a Mn(IV) ground electronic state and an oxygen-centered radical, Mn^{IV}—O·, is another canonical form of Mn^{V}=O.

Product-Determining Processes. On the basis of the mechanism presented in Scheme II, product formation may occur as a result of collapse of the radical pair (alcohol product) or from the free alkyl radicals in solution (alcohol or halogenated product). Possible reaction pathways for the formation of functionalized alkane products from free radicals in solution are given in eq 1.



(1)

A reaction pathway involving an organometallic intermediate resulting from attack at the metal is unlikely to be important with six-coordinate metalloporphyrin complexes of first-row transition metals. A seventh coordination position on the metal of the metalloporphyrin would likely be sterically accessable to only the smallest ligands.[21] The electron-transfer pathway for oxidation of free alkyl radicals can be ruled out for primary substrates on the basis of the *tert*-butylbenzene results (Scheme I). The electron-transfer pathway may, however, be important for tertiary substrates where easily oxidized tertiary radicals are produced. The most likely pathway for ligand-transfer oxidation is the inner-sphere ligand-transfer process involving radical attack at X. This mechanism involves formation of a bridged intermediate [R···X···Mn_{Ox}] which is a facile process for polarizable ligands such as Br and N_3 and to a lesser extent Cl.[22]

Ligand abstraction from iodine may also be important if the ligand X is located on the iodosyl moiety in the starting complex or subsequent intermediates. Visible spectroscopy shows that the ligand X is bound to the metal in the $XMn^{III}TPP$ complexes formed during the reaction. As the following sections will show, ligand transfer from $XMn^{III}TPP$ constitutes the major pathway for RX production.

1. Ligand-Transfer Oxidation of Free Radicals by Manganese Porphyrin Complexes. The ability of free alkyl radicals to abstract the axial ligand from a $XMn^{III}TPP$ complex can be demonstrated by a series of competition reactions. The results listed in Table II show that when 1 equiv of various $XMn^{III}TPP$ complexes is added to the reaction of **1-Cl** or **1-Br** with isobutane or cyclohexane, products derived from the added Mn(III) complexes are formed at the expense of the products derived from the reactant complexes, **1**. Addition of the complex (HO)$Mn^{III}TPP$ apparently causes some decomposition of the reactant complexes, **1**, resulting in a lower yield of products, but the relative yields of ROH vs. RX products indicate a substantial increase in alcohol production. These results show that the free radicals produced by the reaction of **1** with alkanes are indeed capable of abstracting the axial ligand from $XMn^{III}TPP$ complexes.

Transfer of the axial ligand to the alkyl radical in solution would result in reduction of $XMn^{III}TPP$ to the Mn(II) porphyrin. The Mn(II) porphyrin is a d^5 high-spin EPR active species and, if present in sufficient steady-state concentration, should be observable by EPR spectroscopy. The oxidation of alkane substrates or *tert*-butylbenzene by **1-Cl** (Figure 2) does produce a signal in the EPR spectrum which has been identified by three methods as being due to $Mn^{II}TPP$. The observation of $Mn^{II}TPP$ in these reactions confirms the oxidation by ligand transfer from $XMn^{II}TPP$ as a pathway for product formation.

Other complexes in solution that may react with free alkyl radicals by ligand transfer are the reactant, **1**, and the intermediate hydroxymanganese(IV) porphyrin species. The highly reactive oxo intermediates would presumably be sufficiently short-lived to preclude substantial reaction with free alkyl radicals. Ligand abstraction from the reactant, **1**, involves abstraction from the iodine rather than the metal. The high reactivity of the Mn(IV) porphyrins discussed in this paper prevents their use in the competition type experiments used to show ligand transfer from $XMn^{III}TPP$ (vide supra).

Ligand-transfer oxidation of intermediate freely diffusing alkyl radicals would be expected to be faster for Mn(III) (high-spin d^4) than for Mn(IV) (high-spin d^3) complexes on the basis of electronic arguments. Although there is no literature data that define the relative labilities of ligands on Mn(III) vs. Mn(IV) species in similar coordination environments, there is data available for isoelectronic Cr(II) (high-spin d^4) vs. Cr(III) (high-spin d^3) complexes. The rate of exchange of water in the first coordination sphere of $[Cr(H_2O)_6]^{2+}$ is faster by a factor of 10^{15} than for $[Cr(H_2O)_6]^{3+}$.[23] Although the porphyrin ligand can labilize Cr(III) through interaction of the porphyrin π and metal $d(\pi)$ orbitals such that the axial ligands can exchange at rates 10^3–10^4 faster than for other Cr(III) complexes,[24] this is a small effect relative to the factor of 10^{15} derived from d orbital occupancies. Furthermore, the d orbitals of Mn(IV) are lower in energy than for the isoelectronic Cr(III) and less able to interact with the porphyrin ligand π orbitals, a point verified by the "irregular" electronic spectra of Cr(III) porphyrins (d-type hyperporphyrins)[25] as compared to the broadened but relatively normal spectra of Mn(IV) porphyrins.[4] Thus porphyrin ligand labilization of Mn(IV) axial ligands would be quite small ($\ll 10^3$–10^4), and ligand abstraction should be many orders of magnitude faster from Mn(III) than from Mn(IV) porphyrin intermediates. The Mn(IV) porphyrin complexes are also expected to have thermodynamically more stable axial bonds than the d^4 tetragonally distorted $XMn^{III}TPP$ complexes.[26]

The plots of Figure 1 of halogenated product formation in the reaction of 2,3-dimethylbutane with **1-Cl** suggest that halogenated product is produced predominantly by ligand transfer from

(20) Derivatives of iodosylbenzene were synthesized in an analogous manner to that given for iodosylbenzene but using the substituted iodobenzene precursor: cf. Lucas, H. J.; Kennedy, E. R.; Formo, M. W. "Organic Syntheses"; Wiley: New York, 1955; Coll. Vol. 3, pp 483–485.

(21) Seven coordination in metalloporphyrin complexes of first-row transition metals has not been unambiguously established. A pseudo seven-coordinate iron porphyrin has been proposed for the oxygenated form of the capped iron porphyrin of Linard et al. in the presence of 1-MeIm: Linard, J. E.; Ellis, P. E., Jr.; Budge, J. R.; Jones, R. D.; Basolo, F. *J. Am. Chem. Soc.* **1980**, *102*, 1896–1904.

(22) Kochi, J. K. In "Free Radicals"; Wiley: New York, 1973; Vol. 1 p 594.

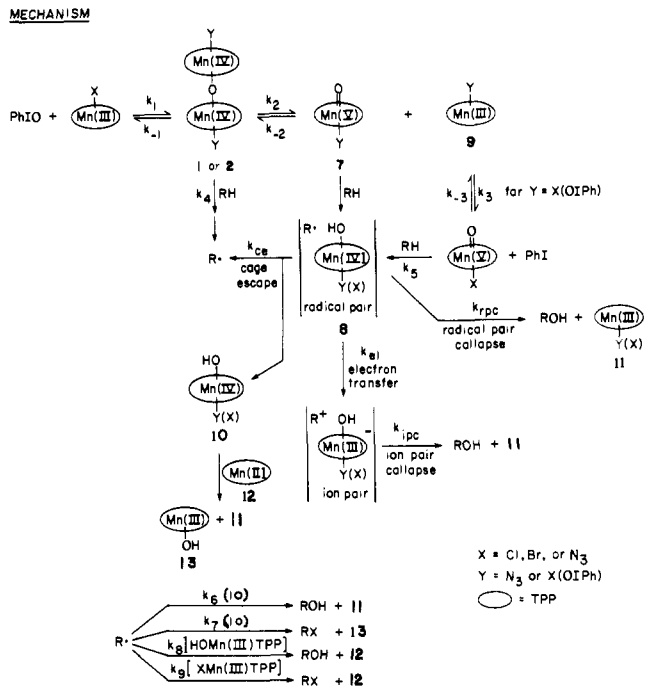
(23) (a) Purcell, K. F.; Kotz, J. C. "An Introduction to Inorganic Chemistry"; Saunders: New York, 1980; p 425. (b) Pearson, R. G.; Ellgen, P. C. "Physical Chemistry, An Advanced Treatise"; Eyring, H., Ed.; Academic Press: New York, 1975; Vol. VII Chapter 5.

(24) Fleischer, E. B.; Krishnamurthy, M. *J. Am. Chem. Soc.* **1971**, *93*, 3784–3786.

(25) Gouterman, M.; Hanson, L. K.; Khalil, G. E.; Leonstra, W. R. *J. Chem. Phys.* **1975**, *62*, 2343–2353.

(26) (a) Kirner, J. F.; Scheidt, W. R. *Inorg. Chem.* **1975**, *14*, 2081–2086. (b) Day, V. W.; Stults, B. R.; Tasset, E. L.; Day, R. O.; Marianelli, R. S. *J. Am. Chem. Soc.* **1974**, *96*, 2650–2652.

Scheme III



$XMn^{III}TPP$, and that until this species is present in sufficient quantity, product formation is not substantial. When the complex $ClMn^{III}TPP$ is added to the reaction, product formation is observed almost immediately and is greater throughout the course of the reaction than that observed in the absence of added $ClMn^{III}TPP$. Since the Mn(IV) starting complex is the predominant species in solution in the early stages of the reaction, we can conclude that ligand transfer from this complex is less favorable than ligand transfer from Mn(III).

2. Ligand-Transfer Oxidation in the Radical Cage. The use of the radical scavenger DPPH in the reactions of **1** with alkanes has indicated that alcohol product can be formed in the radical cage, **8** (Scheme II). Ligand-transfer oxidation in the radical cage, however, involves a hydroxymanganese(IV) porphyrin intermediate which, based on the electronic arguments discussed above, should have low reactivity. Because of the expected low reactivity of Mn(IV) porphyrin complexes toward an inner-sphere ligand-transfer oxidation of the radical, cage escape (k_{ce}, Scheme II) is expected to predominate and alcohol product would result mainly from free radicals in solution. As Table II shows, tertiary alcohol production is relatively invariant with the addition of Mn(III) porphyrin complexes, indicating that tertiary alcohol is produced primarily in the radical cage and not by free alkyl radicals. This result shows that formation of tertiary alcohol product in the radical cage (k_{rpc}, Scheme II) is competitive with diffusion of the radical into solution (k_{ce}, Scheme II). Based on the assumption of the low reactivity of Mn(IV) complexes toward an inner-sphere ligand oxidation process, we must conclude that some other mechanism for alcohol formation in the caged species is operable. The mechanism most in accord with the data is one in which tertiary radicals undergo primarily electron-transfer oxidation to carbonium ions in the radical cage with subsequent ion pair collapse to produce alcohol product, whereas primary radicals undergo predominantly cage escape. The absence of detectable amounts of primary alcohol in these reactions (Table II) supports this conclusion. Because the oxidation of primary radicals is not a facile process, primary alcohol formation in the radical cage does not compete with cage escape and halogenated primary product resulting from ligand-transfer oxidation of the freely diffusing primary radicals is observed. Primary alcohol formation from free radical processes is expected to be minor because of the low concentration in solution of both primary radicals (selectivity ratio of 200:1) and hydroxymanganese porphyrin complexes. These conclusions indicate that an electron-transfer mechanism is the predominant pathway for alcohol formation in the radical cage, with the k_{rpc}/k_{ce} product-determining ratio being determined by the ability of the caged substrate radical to undergo subsequent electron-transfer oxidation.

Conclusions

A complete mechanistic scheme (Scheme III) can now be presented on the basis of the results and conclusions presented thus far. In Scheme III, electron transfer in the radical cage with subsequent ion pair collapse (k_{et}, k_{ipc}) is shown as the major pathway for alcohol formation in the radical cage. A reaction pathway (k_4) involving reaction of the substrate directly with the iodosylbenzene complex **1** is included to represent possible alkane activation pathways other than those involving oxo intermediates such as radical abstraction by iodinanyl radicals. The inner-sphere ligand-transfer oxidation mechanism for alcohol formation in the radical cage (k_{rpc}) is still included as it may constitute a minor pathway in product formation. Also, because of the relative inertness of the manganese(IV) porphyrin complexes toward ligand-transfer oxidation of free radicals, a more probable reaction of these complexes is shown to be oxidation of the $Mn^{II}TPP$ species to give two $Mn^{III}TPP$ complexes. The extent to which the various reaction pathways (k_{et}, k_{ipc}, vs. k_{rpc}, vs. k_{ce}) are important is a function of the substrate radical formed in the reaction. Thus, the low yield of alcohol product observed in the oxidation of *tert*-butylbenzene (Table I) is consistent with the expected relative rates of the various reaction pathways for a primary radical of $k_{ce} > k_{et}$, k_{ipc} and $k_{ce} > k_{rpc}$. The observed products are thus determined mainly by the reactions of free radicals in solution, resulting in the observation of mainly halogenated product due to the predominance of a halogen atom source in solution.

In the activation of hydrocarbons by the complexes **1** and **2**, oxo intermediates resulting from the Mn–O–Mn and Mn–O–I moieties are postulated to be the activating species. The formation of alkyl radicals by abstraction of a hydrogen atom by the activating species indicates the importance of the radical character of these oxo intermediates. The oxo complexes therefore probably have a high degree of triplet character in their ground state and are better represented as Mn^{IV}—O· rather than Mn^{V}=O. Because the formation of product in the oxidation of alkanes by **1** mainly involves free radicals, product distributions can be manipulated in a systematic way through control of the predominant porphyrin species present in solution. Thus, replenishing of the axial ligands X scavenged by the intermediate free radicals would allow the system to become catalytic for RX product formation when an excess of oxidant is present. In this manner, we have recently accomplished the catalytic production of alkyl azides through the introduction of a second aqueous phase containing azide anion.[1a] Work on the scope and mechanism of the activation of alkanes by manganese porphyrins is continuing in our laboratory.

Acknowledgment. Support of this work by the National Science Foundation (Grant No. CHE-7909730) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged.

Registry No. 1 ($X = Cl^-$), 85282-80-0; **1** ($X = Br^-$), 85282-81-1; **2** ($X = N_3^-$), 79775-62-5; $[ClMn^{IV}TPP(Y)]_2O$ (Y = *p*-methoxyiodosylbenzene), 85282-82-2; $[ClMn^{V}TPP(Y)]_2O$ (Y = 2,6-dimethyliodosylbenzene), 85282-83-3; $[BrMn^{III}TPP]$, 55290-32-9; $[N_3Mn^{III}TPP]$, 56413-47-9; $[ClMn^{III}TPP]$, 32195-55-4; $[OHMn^{III}TPP]$, 85135-24-6; cyclohexane, 110-82-7; isobutane, 75-28-5; *tert*-butylbenzene, 98-06-6.