Propyne isomerization, where R' = D and R = H, has indeed been observed, but only in the gas phase at high temperatures, 500–700 °C.[27] Moreover, in this study the isomerization was shown to occur via a cyclopropene intermediate. Allene, CH_2=C=CHD, was only formed as a byproduct. Thus the organometallic and organic analogues appear to differ mechanistically and energetically.

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Dynamics of Reaction of [*meso*-Tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato]iron(III) Hydrate with Various Alkyl Hydroperoxides in Aqueous Solution. 4. Comparison of Kinetic Parameters and D_2O Solvent Isotope Effects

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Abstract: The second-order rate constants (k_{ly}) for the reactions of the alkyl hydroperoxides $(Ph)_2(MeOCO)COOH$ and $(Ph)(Me)_2COOH$ with [*meso*-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato]iron(III) hydrate [(1)Fe^{III}(X)$_2$ (X = H_2O or OH⁻)] have been determined in water over the pH range 1–13 by using the one-electron oxidizable trapping agent 2,2'-azinobis(3-ethylbenzthiazolinesulfonate) (ABTS). The complex pH dependencies of k_{ly} reflect the pH dependency of the structure of reactants and intermediates as shown in Scheme II. Plots of log k_{ly} vs pH were fitted by a steady-state kinetic expression (eq 1) shown previously to describe the pH dependence of the reaction of $(CH_3)_3COOH$ with (1)Fe^{III}(X)$_2$. The dependencies of the rate constants for O–O bond cleavage (k_2 and k_4, Scheme II) of the ligated hydroperoxides YOOH to the pK_a of the leaving group YOH ($\delta(\log k_2)/\delta pK_{aYOH}$ and $\delta(\log k_4)/\delta pK_{aYOH}$) can be isolated from the pH dependencies of the k_{ly} values and are determined to be –0.22 and –0.13, respectively. Thus, the sensitivity of rate constants for the cleavage of the O–O bond of ligated hydroperoxide to its polarity is small. Kinetic deuterium solvent isotope effects for reaction of $(Ph)_2(MeOCO)COOH$ with (1)$Fe^{III}X_2$ have been found to be in accord with those determined previously for $(CH_3)_3COOH$.

Introduction

Acyl and alkyl hydroperoxides are substrates for several important classes of metalloporphyrin-containing enzymes. These include peroxidases, catalases, and the cytochrome P-450 enzymes. The mechanism of oxygen transfer from these hydroperoxides to iron(III) porphyrins is a subject of intense scrutiny. Whereas the consensus of opinion is that oxygen transfer from acyl hydroperoxides to iron(III) porphyrins occurs through heterolytic cleavage of the O–O bond of the hydroperoxide, to yield an iron(IV) porphyrin π-cation radical species and carboxylic acid as products, the primary products of alkyl hydroperoxide reduction have been a subject of much debate.[1–3]

This study is a continuation of an ongoing investigation into the reactions of water-soluble, non-μ-oxo dimer-forming tetraphenyliron(III) porphyrins with alkyl and acyl hydroperoxides in aqueous solution. Previous investigations have shown that the second-order rate constants (k_{ly}) for the reactions of [*meso*-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato]iron(III) hydrate [(1)Fe^{III}(X)$_2$ (X = H_2O or OH⁻)] with acyl or alkyl hydroperoxides, YOOH, exhibit different dependence upon the acidity of the YOH leaving group.[1,4] Plots of log k_{ly} vs the pK_a of YOH

exhibit a definitive break at pK_a of about 11, so that k_{ly} values for the acyl hydroperoxides m-$ClC_6H_4CO_3H$, p-$O_2NC_6H_4CO_3H$, $PhCH_2CO_3H$, and n-$C_5H_{11}CO_3H$ and the alkyl hydroperoxide $Ph_2(CN)COOH$ fall on lines with slopes (β_{lg}) of –0.63, and –0.36 at pH 2.2 and 6.7, respectively, whereas k_{ly} values for the hydroperoxides $(Ph)_2(MeOCO)COOH$, $(Ph)(Me)_2COOH$, HOOH, and $(Me)_3COOH$ fall on separate lines with slopes (β_{lg}) of –0.18 and –0.11 at pH 2.2 and 6.7, respectively.[4] Since heterolytic O–O bond breaking has been established for the reactions of acyl hydroperoxides,[2,5,6] it was proposed that the break in the linear-free energy plot involves a change in mechanism to homolytic O–O bond cleavage with alkyl hydroperoxides. This conclusion is supported by product studies,[6,7] and particularly the stoichiometry of these reactions.[8] That the acyl hydroperoxides and the more acidic alkyl hydroperoxides exhibit a different mechanism than less acidic alkyl hydroperoxides is further supported by results from kinetic studies of the pH dependence of the reactions. Studies of the dynamics of reactions of [(1)$Fe^{III}X_2$, X = OH⁻ or H_2O] with acyl hydroperoxides reveal no pH dependence of these reactions[4] in the pH range 2.2–6.7, whereas the kinetics of the reactions of HOOH and $(Me)_3COOH$ with the water-soluble

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Scheme I[a]

$$ROOH \underset{+H^+}{\overset{K_b \cdot H^+}{\rightleftharpoons}} ROO^- + H^+$$
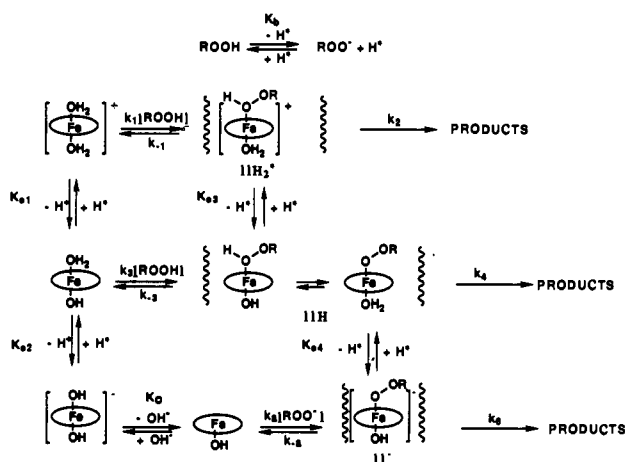
[a] All Fe are in 3+ oxidation state.

non-μ-oxo dimer-forming tetraphenyl porphyrins [(1)Fe^{III}X$_2$, X = OH$^-$ or H$_2$O] and [(2)Fe^{III}X$_2$, X = OH$^-$ or H$_2$O] display pH dependence consistent with a scheme involving the formation of different peroxide-ligated porphyrin intermediates at different pH values.[5,7-10] For the reactions with (Me)$_3$COOH,[5,7,8] a kinetic expression that adequately describes the pH dependence of the second-order rate constants may be derived from Scheme I with the assumption of a steady state in the intermediates II$^-$, IIH, and IIH$_2^+$ (see Discussion). The same expression may be simplified for the situation where all starting materials and intermediates are in rapid equilibrium, to provide an expression that describes the pH dependence of k_{ly} for the reactions of HOOH with (1)-Fe^{III}(X)$_2$ and (2)Fe^{III}(X)$_2$.[9,10]

However, since for the reactions of (Me)$_3$COOH with (1)-Fe^{III}(X)$_2$ and (2)Fe^{III}(X)$_2$, k_{ly} values are seen to be comprised of a large number of rate and equilibrium constants, the dependence of k_{ly} on the pK_a of the YOH leaving group does not necessarily reflect the sensitivity of the O–O bond-breaking step to YOH pK_a. The goal of the present investigation is to isolate the dependencies of the rate constants (k_2 and k_4 in Scheme I) for O–O bond breaking of the porphyrin–hydroperoxide complexes (IIH$_2^+$ and IIH) on the pK_a of the leaving alcohol (pK_{aYOH}). To this end kinetic studies of the pH dependence of the rates of the reactions of the hydroperoxides (Ph)(Me)$_2$COOH and (Ph)$_2$(MeOCO)COOH with [(1)Fe^{III}X$_2$, X = OH$^-$ or H$_2$O] have been carried out and compared with results from a previous study of the reaction of (Me)$_3$COOH. This enabled us to calculate δ(log k_2)/δpK_a and δ(log k_4)/δpK_a for the alkyl hydroperoxides. Solvent isotope studies of the reaction of (Ph)$_2$(MeOCO)COOH with (1)Fe^{III}X$_2$ have also been carried out. Possible mechanisms for the O–O bond cleavage step are discussed in light of the results.

Experimental Section

Materials. Deionized, double glass distilled water was used for all experiments. Buffer and salt solutions were prepared from reagent grade chemicals and either passed over a chelex column (buffers of pH > 7) or extracted with 0.01% dithiazone in dichloromethane to remove any heavy metal contamination. 2,2'-Azinobis(3-ethylbenzthiazoline-6-sulfonic acid), disodium salt (ABTS, disodium salt) was prepared from the commercially available diammonium ABTS (Sigma) as previously described.[8] Deuterium oxide (99.9%) was from Aldrich. Deuterated buffers were prepared by rotary evaporation of aqueous buffer solutions, dissolving the residual salt in D$_2$O and evaporating to dryness. The latter procedure was repeated three times prior to reconstituting the buffer in D$_2$O. Values of pD were determined by the addition of 0.38[11] to the pH meter reading. Cumene hydroperoxide ((Ph)(Me)$_2$COOH) was from Aldrich, and diphenylcarbomethoxymethyl hydroperoxide ((Ph)$_2$(MeO-CO)COOH) was from a previous study.

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Instrumentation. Kinetic studies were conducted with either Perkin-Elmer 553 or Uvikon 810 UV/vis spectrophotometers with cell compartments thermostated at 30 °C. Anaerobic experiments were performed in a glovebox under a nitrogen atmosphere. pH measurements were performed with a Radiometer Model 26 pH-meter. HPLC was performed with an Altex Ultrasphere ODS 5-μm column (4.6 × 250 mm), employing a Hewlett-Packard variable wavelength detector (Model HP1050) interfaced to a Hewlett-Packard HP3392A integrator.

Results

The kinetics of the reactions of (Ph)(Me)$_2$COOH and (Ph)$_2$-(MeOCO)COOH with (1)Fe^{III}(X)$_2$ (30 °C, μ = 0.2) were determined spectrophotometrically, as previously described,[3] by following the increase in absorbance at 660 nm due to oxidation of the trapping agent 2,2'-azinobis(3-ethylbenzthiazoline-6-sulfonic acid), sodium salt (ABTS) to the radical cation (ABTS$^{\bullet+}$). A typical reaction mixture contained (1)Fe^{III}(X)$_2$ in concentrations ranging from 5 × 10^{-7} to 1.2 × 10^{-5} M, in a buffered solution containing 6 × 10^{-3} M ABTS. Buffers employed were ClCH$_2$COO$^-$/ClCH$_2$COOH (pH 1.7-3.7), CH$_3$COO$^-$/CH$_3$COOH (pH 3.7-5.2), H$_2$PO$_4^-$/HPO$_4^{2-}$ (pH 5.7-7.8), HCO$_3^-$/CO$_3^{2-}$ (pH 8.9-10.5), and H$_2$O/HO$^-$ (above pH 10.5). Reactions were initiated by addition of hydroperoxide to a final concentration of 6 × 10^{-5} M. The appearance of ABTS$^{\bullet+}$ followed the first-order rate law to completion of reactions between pH 4.0 and 8.0. At pH values <4 and >8 the kinetics were somewhat more complex. At low pH values, ABTS is oxidized to ABTS$^{\bullet+}$ in the presence of O$_2$. This problem was minimized by running the reactions in a glovebox under nitrogen atmosphere. On occasion, traces of O$_2$ remaining in solution brought about a small zero-order drift, which was corrected for by use of a program for simultaneous zero- and first-order reactions to fit the plot of A_{660} vs time. At high pH values, ABTS$^{\bullet+}$ is increasingly susceptible to oxidation to the colorless ABTS^{2+}. In these cases the first-order rate constants (k_{obsd}) for ABTS → ABTS$^{\bullet+}$ → ABTS^{2+} were obtained by the fitting of A_{660} vs time plots to the appropriate rate expression for two sequential first-order reactions. Such fitting of kinetic data was carried out at each pH investigated, using five to six values of [(1)Fe^{III}(X)$_2$], over a tenfold concentration range.

At all pH values, the rate constants (k_{obsd}) for ABTS → ABTS$^{\bullet+}$ were linearly dependent on (1)Fe^{III}(X)$_2$. Second-order rate constants (k_{ly}^H) were obtained from the slopes of the linear plots of k_{obsd} vs [(1)Fe^{III}(X)$_2$]. At pH's below 3 and above 10, plots of k_{obsd} vs [(1)Fe^{III}(X)$_2$] were found to have nonzero intercepts. This indicates that there is a slow decomposition of hydroperoxide which is independent of the presence of iron(III) porphyrin. No buffer catalysis was detected with ClCH$_2$COO$^-$/ClCH$_2$COOH, CH$_3$COO$^-$/CH$_3$COOH, H$_2$PO$_4^-$/HPO$_4^{2-}$, and HCO$_3^-$/CO$_3^{2-}$ buffers. Twelve values of k_{ly}^H, for the reaction of cumene hydroperoxide with [(1)Fe^{III}(X)$_2$], were determined at pH values ranging from 1.7 to 12.6. With diphenylcarbomethoxymethyl hydroperoxide, 18 values of k_{ly} were determined between pH 1.05 and 11.5.

The determination of first- and second-order rate constants in D$_2$O (k_{obsd}^D and k_{ly}^D) **of the reaction of (Ph)$_2$(MeOCO)COOD with [(1)Fe^{III}(X)$_2$]** were carried out under the same conditions as described for H$_2$O. Preparation of deuterated buffers is described in the Experimental Section. Rate constants were determined at eight different pD values ranging from 2.0 to 10.3. It was not possible to obtain k_{ly}^D above pD 10.3 by this method, due to a solvent kinetic isotope effect such that the rates of oxidation of ABTS$^{\bullet+}$ → ABTS^{2+} approach the k_{obsd}^D values for ABTS → ABTS$^{\bullet+}$ so that very little change in A_{660} is seen.

Products formed from the reaction of (1)Fe^{III}(X)$_2$ with (Ph)$_2$(MeOCO)COOH were determined by HPLC. Products formed, at pH 2.7, 6.7, 8.9, and 12.5 are provided in Table I. Without ABTS present, over the pH range 2.7-8.9, 78-82% of the total mass of hydroperoxide was accounted for by benzophenone (28-34%) and (Ph)$_2$(MeOCO)COH (47-50%). At higher pH values (Ph)$_2$(MeOCO)COH was not detected, and enhanced yields of benzophenone (52%) were found.

At high concentrations of ABTS both benzophenone and (Ph)$_2$(MeOCO)COH were again identified as products of the

Table I. Yields of $(Ph)_2(MeOCO)COH$ and $(Ph)_2C=O$ Obtained from HPLC Analysis of Spent Reaction Mixtures from the Reactions of $[(1)Fe^{III}(X)_2]$ $(1.2 \times 10^{-4}$ M) and $(Ph)_2(MeOCO)COOH$ $(1.2 \times 10^{-3}$ M) with (A) 10^{-2} M [ABTS] and (B) No ABTS Present

pH	$(Ph)_2C=O$ (%)		$(Ph)_2(MeOCO)COH$ (%)	
	A	B	A	B
12.5	32	52		
8.9	34	30	74	47
6.7	36	28	51	49
2.7	22	33	88	48

Scheme II

Path I

Path II

Path III

Path IV
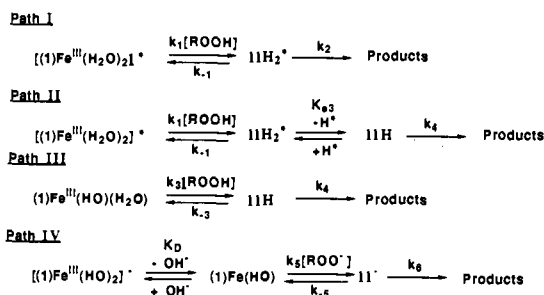
reaction of $(1)Fe^{III}(X)_2$ with $(Ph)_2(MeOCO)COOH$ at pH 2.7, 6.7, 8.9, and 12.5 (Table I). The concentration of ABTS used was 1×10^{-2} M. With 1×10^{-2} M ABTS, in the reaction of $(1)Fe^{III}(X)_2$ with $(Me)_3COOH$ and with $(Ph)(Me)_2COOH$, all easily reduced species that may be formed were found to be trapped.[5] However, in the present study, substantial concentrations of benzophenone (22–36%) were found as product. Higher concentrations (50–90%) of $(Ph)_2(MeOCO)COH$ were also observed in the presence of ABTS. Estimation of $(Ph)_2(MeO-CO)COH$ by HPLC under these conditions was complicated by trailing baselines resulting from the intense signal from ABTS and are only good to within 10%.

Discussion

The objective of the present investigation has been to determine the influence of the R^1, R^2, and R^3 substituents of $(R^1)(R^2)(R^3)COOH$ on the pH dependence of its reaction with iron(III) porphyrin [meso-tetrakis(2,6-dimethyl-3-sulfonato-phenyl)porphinato]iron(III) hydrate $[(1)Fe^{III}(X)_2$ (X = Y_2O or YO^-, Y = H or D)]. The dynamic parameters have been determined with $(Ph)(Me)_2COOH$ and $(Ph)_2(MeOCO)COOH$ and compared to those of $(Me)_3COOH$ from a previous investigation.[8] The kinetic studies were in H_2O and D_2O at 30 °C and $\mu = 0.2$ with $NaNO_3$.

The pH dependences of the second-order rate constants (k_{1y}) for the reaction of the hydroperoxides $(Ph)_2(MeOCO)COOH$ and $(Ph)(Me)_2COOH$ with $(1)Fe^{III}(X)_2$ (from this study) and of the reaction of $(Me)_3COOH$ with $(1)Fe^{III}(X)_2$ (from a previous study)[8] are shown in Figure 1. The data points in Figure 1 are experimental, and the lines are generated from eq 1 with the values of constants reported in Table II. Equation 1 is derivable from

$$k_{1y} = A + B + C$$

$$A = \frac{k_2 k_1}{(k_2 + k_{-1})} \cdot \frac{a_H}{(a_H + K_{a1})}$$

$$B = \frac{\frac{k_2 k_1}{(k_2 + k_{-1})} \left\{ \frac{k_4 K_{a3} a_H^2}{k_2} + \frac{k_4 k_3 K_{a3} K_{a1} a_H}{k_2 k_1} \right\}}{\left\{ a_H^2 + \frac{(k_4 + k_{-3})a_H K_{a3}}{(k_2 + k_{-1})} + \frac{(k_6 + k_{-5})K_{a3} K_{a4}}{(k_2 + k_{-1})} \right\} (a_H + K_{a1})}$$

$$C = \frac{\left\{ \frac{k_6 k_5 K_D K_{a2} K_b}{(k_6 + k_{-5}) K_w} \right\} a_H}{(a_H + K_{a2})(K_b + a_H)} \tag{1}$$

Table II. Values of Rate and Equilibrium Constants Obtained from the Fitting of Eq 1 to the Experimental Points in Figure 1

kinetic terms (units in mol, s)	values of determined constants in reaction of $(1)Fe^{III}(X)_2$ with		
	$(Me)_3$-$COOH^a$	$(Ph)(Me)_2$-$COOH$	$(Ph)_2$-$(MeOCO)COOH$
$k_1 k_2/(k_2 + k_{-1})$	5.0	3.0	56.7
$(k_4/k_2)K_{a3}$	1.4×10^{-4}	4.5×10^{-4}	2.5×10^{-4}
k_3/k_1	0.44	0.42	0.09
$(k_4 + k_{-3})K_{a3}/$ $(k_2 + k_{-1})$	5.5×10^{-7}	7.7×10^{-7}	3.0×10^{-6}
$(k_6 + k_{-5})K_{a4}/$ $(k_4 + k_{-3})$	1.1×10^{-8}	1.0×10^{-8}	4.8×10^{-9}
K_{a1}	1.8×10^{-7}	1.8×10^{-7}	1.8×10^{-7}
$k_6 k_5 K_D/(k_6 + k_{-5})$	71.1	215	154
K_{a2}	1.2×10^{-11}	2.76×10^{-12}	2.6×10^{-12}
K_b	1.6×10^{-13}	2.0×10^{-13}	4.0×10^{-13}

^{a} From previous study.[8]

the reaction sequences of Scheme I, where the reaction proceeds through paths I, II, III, and IV as shown in Scheme II. Steady-state conditions for the intermediates IIH_2^+, IIH, and II^- were assumed. The development of eq 1 has been discussed in a previous manuscript dealing with the reaction of $(Me)_3COOH$ with meso-tetrakis(2,6-dichloro-3-sulfonatophenyl)iron(III) hydrate $[(2)Fe^{III}(X)_2]$.[7] Equation 1 has previously been shown to fit the pH dependence of the reactions of $(Me)_3COOH$ with $[(1)Fe^{III}(X)_2]$[8] and with $[(2)Fe^{III}(X)_2]$[7] and is now seen to adequately describe the pH dependence of the reactions of $(Ph)_2$-$(MeOCO)COOH$ and $(Ph)(Me)_2COOH$ with $(1)Fe^{III}(X)_2$.

The pK_{a1} for the $H^+(D^+)$ ionization of the X (= H_2O, D_2O) ligands of $(1)Fe^{III}(X)_2$ (pK_{a1}) were determined previously,[8] and the pK_a of cumene hydroperoxide $(pK_b = 12.6)$ has been reported in the literature.[12] All other constant terms in Table II were obtained by iterative fitting of eq 1 to the experimental log k_{1y} points. The value of pK_b, used for fitting the pH dependence of k_{1y} for the reaction of $(Ph)_2(MeOCO)COOH$ with $(1)Fe^{III}(X)_2$, is consistent with prediction from studies[13] of the dependence of the pK_a values of alkyl hydroperoxides on structure.

The kinetic parameters obtained for the reactions of $(Ph)_2$-$(MeOCO)COOH$, $(Ph)(Me)_2COOH$, and $(Me)_3COOH$ with $(1)Fe^{III}(X)_2$ are best compared by taking into account the inductive effects of the $-Me$, $-Ph$, and $-CO_2Me$ substituents. The values of σ^I are $-Me$, -0.05; $-Ph$, 0.1; and $-CO_2Me$, 0.34.[14] Thus $\sum \sigma^I$ for the hydroperoxides are $(Me)_3COOH$, -0.15; (Ph)-$(Me)_2COOH$, 0.0; and $(Ph)_2(MeOCO)COOH$, 0.54. If hydroperoxide O–O bond cleavage is heterolytic, the direct product of the hydroperoxide reactions with $(1)Fe^{III}(X)_2$ will be the corresponding alcohols or alkoxide ions. One should expect, in this instance, a linear relationship between the pK_a values of the corresponding alcohols and log k_{1y} at a given value of pH(D). The value of ρ^I for substituted methanols is known to be -8.2 to -8.4[13,15] and the pK_a of MeOH is 15.5[16] such that the pK_a values may be calculated as $(Ph)_2(MeOCO)COH$, 11.1; $(Ph)(Me)_2COH$, 15.5; and $(Me)_3COH$, 16.7. If heterolytic O–O bond scission is involved in the breakdown of the iron(III) porphyrin ligated hydroperoxide, the order of the rate constants for this step of the reaction should then be $(Ph)_2(MeOCO)COOH \gg (Ph)(Me)_2COOH > (Me)_3COOH$, whereas with homolytic scission the rate constants

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(13) Richardson, W. H.; Hodge, V. F. *J. Org. Chem.* **1970**, *35*, 4012. pK_a values of tertiary alkyl hydroperoxides were correlated by the Ingold–Taft equation to give $pK_a = (-0.51 \pm 0.07)\sigma^* + 13.13 \pm 0.02$ and yields $pK_a = 12.76 \pm 0.07$ for $(Ph)_2(MeOCO)COOH$ in 40% aqueous methanol. This corrects to a pK_a of 12.3 ± 0.07 in H_2O. Value of pK_a used to fit experimental data was 12.4.

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(17) The constant K_{a3} pertains to the acid dissociation of $(Ph)_2(MeO-CO)COOH$ when ligated to the iron(III) porphyrin (Scheme I). If the acid dissociation constants of the alkyl hydroperoxides display the same dependence on structure whether or not the hydroperoxide is ligated to the porphyrin, then $r = \delta(\log K_{a3})/\delta pK_{aYOH} = \delta(\log K_b)/\delta pK_{aYOH} = -0.07$, based on the values of K_b in Table II.

Iron(III) Hydrate with Alkyl Peroxides
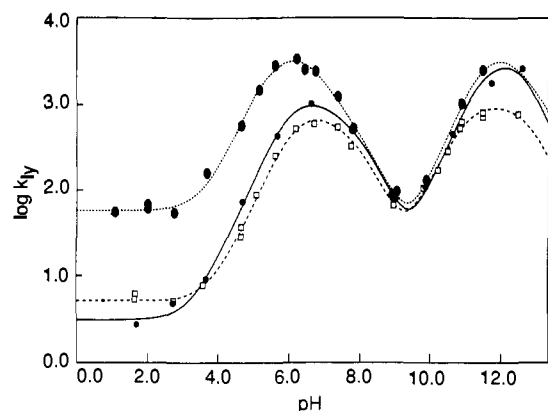
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Figure 1. Plots of k_{ly}^H for the reactions of $(R^1)(R^2)(R^3)COOH$ species with $[(1)Fe^{III}(X)_2$ (X = H_2O or HO^-)] vs pH; (●) ($R^1 = R^2 = Ph$, $R^3 = CO_2Me$), (●) ($R^1 = R^2 = Me$, $R^3 = Ph$), (□) ($R^1 = R^2 = R^3 = Me$). The points are experimental, and the lines were computer-generated by iterative fitting of the points to eq 1. The kinetic studies were in H_2O at 30 °C and μ = 0.2 with $NaNO_3$. The values of constants that provided the optimal fits shown are provided in Table II.

should be much the same.

Inspection of Figure 1 shows that the pH-rate profiles for the reactions of $(CH_3)_3COOH$ and $(Ph)(Me)_2COOH$ are virtually identical in the pH range 2–10 and differ only a little at high pH. The pH-rate profile for the reaction of $(Ph)_2(MeOCO)COOH$ with $(1)Fe^{III}(X)_2$ is almost superimposed on the profile for the reaction of $(Ph)(Me)_2COOH$ with $(1)Fe^{III}(X)_2$ in the pH range 8–12. Below pH 8, the apparent second-order rate constants for reaction (k_{ly}) of $(1)Fe^{III}(X)_2$ with $(Ph)_2(MeOCO)COOH$ are significantly higher than with the other two hydroperoxides. Since both steady-state ligation of hydroperoxide and cleavage of hydroperoxide O–O linkage are embodied in the value of k_{ly} (Scheme I), the rate enhancement with $(Ph)_2(MeOCO)COOH$ below pH 8 could result from either step being facilitated.

The term $k_1k_2/(k_2 + k_{-1})$ of eq 1 represents the k_{ly} between pH 1–4 (reactions of path I of Scheme II). The term $k_1k_2/(k_2 + k_{-1})$ is seen (from Table II) to have similar numerical values for $(Me)_3COOH$ and $(Ph)(Me)_2COOH$ but an order of magnitude larger value for $(Ph)_2(MeOCO)COOH$. If k_2 is rate-limiting at low pH, $k_{-1} > k_2$ such that $k_1k_2/(k_2 + k_{-1}) \approx (k_1/k_{-1})k_2$.[7] Thus any change in log $(k_1/k_{-1})k_2$ with hydroperoxide structure is a sum of the changes in log (k_1/k_{-1}) and in log k_2. The equilibrium constant for hydroperoxide ligation (k_1/k_{-1}) is expected to increase with an increase in the pK_a of alkyl hydroperoxide (pK_b in Table I), whereas the rate constant for O–O bond breaking (k_2) would be expected to decrease with an increase in the pK_a of the leaving alcohol (pK_{aYOH}). The pK_b values change by only 0.4 units in going from the least electron-deficient $(Me)_3COOH$ to the most electron-deficient $(Ph)_2(MeOCO)$-COOH, whereas pK_{aYOH} values change by 5.6 units. Thus, the change in (k_1/k_{-1}) is not expected to contribute much to the change in $(k_1/k_{-1})k_2$, on going from the most to the least acidic alkyl hydroperoxide. The change in k_{ly}, in this pH range, must be attributed, in the main, to an enhancement of the rate constant (k_2) for decomposition of complexed peroxide (intermediate IIH_2^+ of Scheme I) to products. Thus the slope of the least-squares fit of log $\{k_1k_2/(k_2 + k_{-1})\}$ vs pH provides a measure of the sensitivity of k_2 to the structure of the hydroperoxide. Such slope is equal to –0.22. Thus, though the order of reactivity is $(Ph)_2(MeO-CO)COOH > (Ph)(Me)_2COOH \equiv (Me)_3COOH$, the sensitivity to the leaving tendency of ROH or RO^- is quite small. This result would be in accord with O–O bond homolysis or O–O bond heterolysis with an early transition state. The slope for log k_{ly} vs pH for heterolytic O–O bond scission, in the reactions of acyl hydroperoxides with $(1)Fe^{III}(X)_2$ in this pH range, is equal to –0.63.[4]

For the ascending portion of the bell in the neutral pH range,

Table III. Values of Rate and Equilibrium Constants Obtained from the Fitting of Eq 1 to the Experimental Points in Figure 2

kinetic terms (units in mol, s)	values of determined constants in reaction of $(1)Fe^{III}(X)_2$ with $(Ph)_2(MeOCO)COOD$ in D_2O	isotope effects (k^H/k^D)
$k_1k_2/(k_2 + k_{-1})$	21.7	2.6
$(k_4/k_2)K_{a3}$	5.1×10^{-4}	0.5
k_3/k_1	12.3	
$(k_4 + k_{-3})K_{a3}/(k_2 + k_{-1})$	9×10^{-6}	
$(k_6 + k_{-5})K_{a4}/(k_4 + k_{-3})$	4×10^{-7}	
K_{a1}	5.6×10^{-8}	3.2

the numerical value of $(k_4/k_2)K_{a3}$ does not differ significantly for the three hydroperoxide reactions (Table II). A plot of log $(k_4/k_2)K_{a3} = \{(\log k_4 - \log k_2) + \log K_{a3}\}$ vs pH yields a slope of 0.017. If log $k_4 = mpK_{aYOH} + x$, log $k_2 = npK_{aYOH} + y$ and log $K_{a3} = rpK_{aYOH} + z$ then $(m - n + r) = 0.017$. Since n has previously been deduced to be –0.22, and $r \sim -0.07$,[17] it follows that $m = -0.13$. Thus, though the order of reactivity is again $(Ph)_2(MeOCO)COOH > (Ph)(Me)_2COOH \equiv (Me)_3COOH$ the sensitivity to the leaving tendency of ROH or RO^- is even smaller than at acid pH. In the neutral pH range, a slope of –0.36 is obtained from a log k_{ly} vs pH plot for reactions of acyl hydroperoxides with $(1)Fe^{III}(X)_2$.[4]

The only other isolable kinetic term in Table II, that displays any significant dependence on the nature of the hydroperoxide, is $(k_4 + k_{-3})/(k_2 + k_{-1})K_{a3}$. This term is 5- and 7-fold greater with $(Ph)_2(MeOCO)COOH$ as compared to $(Ph)(Me)_2COOH$ and $(Me)_3COOH$, respectively. When corrected for the expected 2-fold difference in the K_a of ligated hydroperoxide (K_{a3}), only a 2–3-fold difference in values for $(k_4 + k_{-3})/(k_2 + k_{-1})$ remains. No significance is ascribed to this small numerical ratio since it amounts to a value of $\Delta\Delta G^{\ddagger}$ of only 400–600 cal mol^{-1}.

Thus the only noticeable difference in the rate constants for O–O bond cleavage of $(1)Fe^{III}(X)_2$ ligated $(Ph)_2(MeOCO)COOH$ as compared to ligated $(Ph)(Me)_2COOH$ and $(Me)_3COOH$ is found in the pH region 1–7 which involves the rate constants k_2 and k_4 of pathways I and II of Scheme II. However, the dependences of k_2 and k_4 upon the polarity of the O–O bond (i.e., pK_a of $(R^1)(R^2)(R^3)COH$ leaving group) is quite modest.

Comparison of the Kinetic Parameters Obtained for the Reaction of $(Ph)_2(MeOCO)COOH(D)$ with $(1)Fe^{III}(X)_2$ in H_2O and D_2O. The pH dependences of k_{ly}^H and k_{ly}^D are shown in Figure 2. Values of $k_{ly}^{H(D)}$ are composed of several terms, which must be resolved in order to assign isotope effects to individual steps of the reactions of Scheme II. The kinetic parameters required to fit eq 1 to $k_{ly}^{H(D)}$ for the reaction of $(Ph)_2(MeOCO)COOH(D)$ with $(1)Fe^{III}(X)_2$ in H_2O and in D_2O (where X = Y_2O or YO^- and Y = H or D) are presented in Table III. Due to the limited pH range in which it was possible to acquire data for the reaction in D_2O, only the two terms $(\{k_1k_2/(k_2 + k_{-1})\}$ and $\{k_4K_{a3}/k_2\})$ of eq 1 have unique solutions.
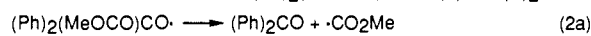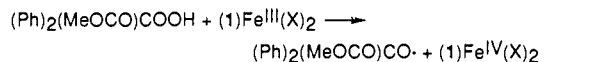
The kinetic isotope ratio $(k_1^H/k_1^D)(k_2^H/k_2^D)(k_2^D + k_{-1}^D)/(k_2^H + k_{-1}^H) = 2.6$ pertains to the kinetic isotope effect of the pH independent reaction below pH 3. The constants k_1 and k_{-1} relate to $(Ph)_2(MeOCO)COOH(D)$ ligation to and dissociation from the iron(III) porphyrin. Therefore, k_1^H/k_1^D and k_{-1}^H/k_{-1}^D represent secondary isotope effects and should approximate unity. Also, k_2 is a commitment step such that $k_{-1} \gg k_2$. It follows that $(k_2^D + k_{-1}^D)/(k_2^H + k_{-1}^H) \approx k_{-1}^D/k_{-1}^H \approx 1$. Therefore, the breakdown of $[(1)Fe^{III}(H_2O)((Ph)_2(MeOCO)COOH)]$ (pathway I of Scheme II) to products at low pH is associated with a solvent isotope effect $(k_2^H/k_2^D) \approx 2.6$. A deuterium solvent kinetic isotope effect of this magnitude is expected for a reaction which involves H^+/D^+ or H^*/D^* transfer to and from oxygen.

The term $\{k_4K_{a3}/k_2\}$ describes the ascending leg of the bell at intermediate pH in the plot of log k_{ly} vs pH. The isotope effect of 0.5 (Table III) pertains to the fraction $(k_4^H/k_4^D)(k_2^D/k_2^H)(K_{a3}^H/K_{a3}^D)$. We have earlier deduced that $(k_2^H/k_2^D) = 2.6$. Thus, $(k_4^H/k_4^D)(K_{a3}^H/K_{a3}^D) = 1.3$. Since pK_{a1} and the kinetically apparent pK_{a3} differ by less than 1 and $K_{a1}^H/K_{a1}^D = 3.2$, it is reasonable to expect $K_{a3}^H/K_{a3}^D \geq 1.3$, such that $(k_4^H/k_4^D) \leq 1$.
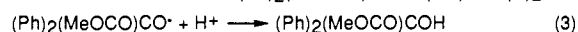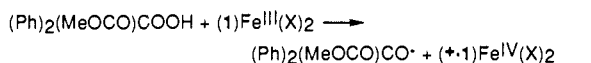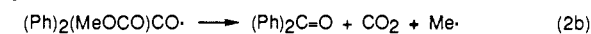
(18) (a) Richardson, W. H.; Smith, R. S.; Snyder, G.; Anderson, B.; Kranz, G. L. *J. Org. Chem.* **1972**, *37*, 3915. (b) Avramoff, M.; Sprinzak, Y. *J. Am. Chem. Soc.* **1963**, *85*, 1655.

Thus there appears to be no isotope effect on the breakdown of $[(1)Fe^{III}(HO)((Ph)_2(MeOCO)COOH)/(1)Fe^{III}(H_2O)((Ph)_2-(MeOCO)COO)]$ at intermediate pH values. The same conclusions were arrived at for the reaction of $(Me)_3COOH$ with $(1)Fe^{III}(X)_2$.[8] Thus, the only kinetic solvent deuterium isotope effect $(k_2^H/k_2^D = 2.6)$ is seen for reaction I of Scheme II.

The products of reaction of $(1)Fe^{III}(X)_2$ with $(Ph)_2(MeO-CO)COOH$ in the presence and absence of the trapping agent ABTS are $(Ph)_2(MeOCO)COH$ and $(Ph)_2C=O$. These products account for 80–100% of hydroperoxide between pH 2.7–8.9 (Table I). Product formation may be discussed in terms of eq 2 vs 3 and following reactions. The fragmentation reaction of eq 2a has been
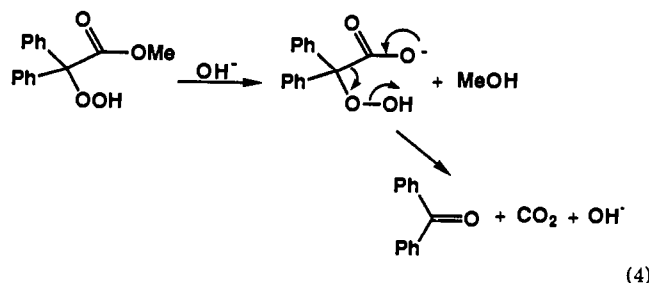
$(Ph)_2(MeOCO)COOH + (1)Fe^{III}(X)_2 \longrightarrow$

$(Ph)_2(MeOCO)CO\cdot + (1)Fe^{IV}(X)_2$

$(Ph)_2(MeOCO)CO\cdot \longrightarrow (Ph)_2CO + \cdot CO_2Me$ (2a)

or

$(Ph)_2(MeOCO)CO\cdot \longrightarrow (Ph)_2C=O + CO_2 + Me\cdot$ (2b)

$(Ph)_2(MeOCO)COOH + (1)Fe^{III}(X)_2 \longrightarrow$

$(Ph)_2(MeOCO)CO\cdot + (+\cdot1)Fe^{IV}(X)_2$

$(Ph)_2(MeOCO)CO\cdot + H^+ \longrightarrow (Ph)_2(MeOCO)COH$ (3)

observed with cumyl hydroperoxide $[(Me)_2(Ph)CO\cdot \rightarrow (Ph)-(Me)C=O + Me\cdot]$ and *tert*-butyl hydroperoxide $\{(Me)_3O\cdot \rightarrow (Me)_2C=O + Me\cdot]$, and the yields of products are in accord with proposed mechanisms.[5] Yields of $(Ph)_2C=O$ are insensitive to pH between 2.7 and 8.9 and unaffected by the inclusion of ABTS in the reaction mixture. This may find an explanation by the assumption and the rearrangement of $(Ph)_2(MeOCO)CO\cdot$ to $(Ph)_2CO$ occurs with such a rate constant that the intermediate $(Ph)_2(MeOCO)CO\cdot$ is not trapped by ABTS at 10^{-2} M. If this is so, O–O bond homolysis must be important throughout the pH range employed since ~30% yields of $(Ph)_2CO$ are obtained.

Between pH values of 2.7 and 8.9 the yields of $(Ph)_2(MeO-CO)COH$ are insensitive to pH in the absence of ABTS, but inclusion of 10^{-2} M ABTS leads to an increase in the yields of $(Ph)_2(MeOCO)COH$ at pH 2.7 and 8.9. These increased yields of $(Ph)_2(MeOCO)COH$ are not accompanied by decreased yield of $(Ph)_2C=O$. We have no explanation for this observation. The alcohol $(Ph)_2(MeOCO)COH$ is not a stable entity. Thus, in spent reaction solutions the concentration of $(Ph)_2(MeOCO)COH$ decreases with time, especially at high pH. This decomposition of $(Ph)_2(MeOCO)COH$ is not associated with an increase in $(Ph)_2C=O$. We do not consider the reported product yields to be quantitatively useful.

At pH 12.5, *no* $(Ph)_2(MeOCO)COH$ is found, and the yields of $(Ph)_2C=O$ are greater in the absence of ABTS. That $(Ph)_2C=O$ formation does not occur by $(Ph)_2(MeOCO)CO^-$ decomposition was shown by spectrophotometrically monitoring a solution of $(Ph)_2(MeOCO)COH$ at pH ~11 at the absorption maximum of $(Ph)_2C=O$. Formation of $(Ph)_2C=O$ was not observed over a 48-h period of time. The enhanced yields of $(Ph)_2C=O$, at alkaline pH, are attributed to non-porphyrin-catalyzed fragmentation of the hydroperoxide (eq 4). Such a mechanism for hydroxide-catalyzed decomposition of $(Ph)_2-$

[structure: Ph, Ph, with O, OMe, OOH groups, arrow OH⁻, → structure with O, O⁻, O–OH + MeOH, then arrow down to Ph, Ph structure =O + CO₂ + OH⁻]

(4)

$(MeOCO)COOH$, has been previously established.[18] In the presence of ABTS the porphyrin-catalyzed reaction is expected to be faster, and hence little contribution from non-porphyrin-catalyzed decomposition of $(Ph)_2(MeOCO)COOH$ is expected.

Mechanisms of Reactions. From Figure 1 the plots of log k_{ly} vs pH for the reactions of $(1)Fe^{III}(X)_2$ with $(Ph)(Me)_2COOH$
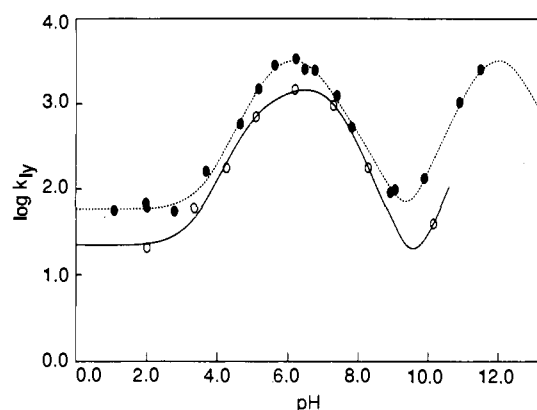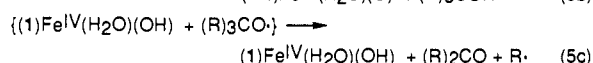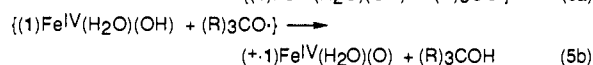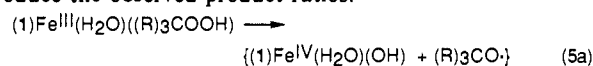

Figure 2. Plots of k_{ly}^H (●) and k_{ly}^D (○) for the reactions of $(Ph)_2-(MeOCO)COOH(D)$ with $[(1)Fe^{III}(X)_2$ (X = Y_2O or YO⁻, Y = H or D)] in H_2O or D_2O vs pH(D). The points are experimental, and the lines were computer-generated by iterative fitting of the points to eq 1. The kinetic studies were in H_2O and D_2O at 30 °C and $\mu = 0.2$ with $NaNO_3$. The values of constants that provided the optimal fits shown are provided in Table III.

and $(Me)_3COOH$ are almost identical. The pH profile for the reaction of $(1)Fe^{III}(X)_2$ with $(Ph)_2(MeOCO)COOH$ is also very similar. However, k_{ly} values, at the plateau region at low pH, for $(Ph)_2(MeOCO)COOH$ are ~10-fold higher than with $(Ph)(Me)_2COOH$ and $(Me)_3COOH$. At the top of the first "bell" k_{ly} for $(Ph)_2(MeOCO)COOH$ is 3–5-fold greater than for $(Ph)(Me)_2COOH$ and $(Me)_3COOH$. At higher pH values there is little difference in the k_{ly} values of the three peroxides. Thus, the dynamics for the reactions with the three peroxides are very similar to each other and virtually identical with the two less acidic hydroperoxides.

The dependence of k_{ly} on pK_a of $(R^1)(R^2)(R^3)COH$ for the reactions of $(Ph)_2(MeOCO)COOH$, $(Ph)(Me)_2COOH$, and $(Me)_3COOH$ with $(1)Fe^{III}(X)_2$ had been determined at pH values 2.2 and 6.7 in a previous study and values of $\delta(\log k_{ly})/\delta pK_a$ were determined to be -0.18 and 0.11, respectively.[4] These k_{ly} values are pH dependent and are a combination of several rate terms at each pH. The determination of the pH dependence of k_{ly} for each peroxide has now been carried out, and the change in the rate constants for the decomposition of iron(III) porphyrin ligated hydroperoxide species are isolated from the change in the general expressions for the formation and decomposition of these species. This provides $\delta(\log k_2)/\delta pK_a = -0.22$ and $\delta(\log k_4)/\delta pK_a = -0.13$. This validates our earlier study.[4] Thus the sensitivity of rate constants for decomposition of IIH and IIH_2 of Scheme I (pH region 1–7) to the polarity of the O–O bond is small. Of the two rate constants only k_2 exhibits a solvent deuterium kinetic isotope effect $(k_2^H/k_2^D = 2.6)$. An essentially identical deuterium solvent isotope effect of $(k_2^H/k_2^D \approx 2.7)$ was obtained for the reaction of $(Me)_3COOH$ with $(1)Fe^{III}(X)_2$ at low pH.[8] Buffer catalysis is not observed in the reaction of $(Me)_3COOH$, $(Ph)(Me)_2COOH$, or $(Ph)_2(MeOCO)COOH$ with $(1)Fe^{III}(X)_2$, and the reactions are not catalyzed by H_3O^+ in the pH acidity range 1–4. The presence of a solvent kinetic isotope effect and the lack of buffer catalysis may be reconciled, as previously proposed,[8] by the mechanism of eqs 5a and b (where homolysis and H⁺ transfer are both partially rate controlling). Fragmentation of the caged $(R)_3CO\cdot$ (5c) may then compete with hydrogen abstraction to produce the observed product ratios.

$(1)Fe^{III}(H_2O)((R)_3COOH) \longrightarrow$

$\{(1)Fe^{IV}(H_2O)(OH) + (R)_3CO\cdot\}$ (5a)

$\{(1)Fe^{IV}(H_2O)(OH) + (R)_3CO\cdot\} \longrightarrow$

$(+\cdot1)Fe^{IV}(H_2O)(O) + (R)_3COH$ (5b)

$\{(1)Fe^{IV}(H_2O)(OH) + (R)_3CO\cdot\} \longrightarrow$

$(1)Fe^{IV}(H_2O)(OH) + (R)_2CO + R\cdot$ (5c)