Reaction of (meso-Tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato)-iron(III) Hydrate with Various Acyl and Alkyl Hydroperoxides in Aqueous Solution

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Abstract: The reactions of (meso-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato)iron(III) hydrate [(1)Fe^{III}(H$_2$O)(X), where X = HO$^-$ or H$_2$O] with the YOOH species m-ClC$_6$H$_4$CO$_3$H, p-O$_2$NC$_6$H$_4$CO$_3$H, PhCH$_2$CO$_3$H, n-C$_5$H$_{11}$CO$_3$H, Ph$_2$C(CO$_2$CH$_3$)OOH, Ph$_2$C(CN)OOH, PhC(CH$_3$)$_2$OOH, and t-BuOOH have been investigated in aqueous solution. It was determined for all reactions that oxygen transfer is first order in both [YOOH] and [(1)Fe^{III}(H$_2$O)(X)] by following the reactions with alkyl hydroperoxides, through trapping of intermediate oxidants with 2,2′-azinobis(3-ethylbenzthiazolinesulfonic acid) (ABTS), and acyl hydroperoxides, by monitoring the decrease in the Soret absorbance. The reactions involving alkyl hydroperoxides are not subject to general catalysis by oxyanion bases or their conjugate acids. With ABTS as a trap [with PhC(CH$_3$)$_2$OOH and t-BuOOH], or by following the decrease in the Soret absorbance [with Ph$_2$C(CN)OOH], general catalysis was not observed with the nonligating nitrogen base 2,4,6-trimethylpyridine and its conjugate acid. The second-order rate constants (k_{ly}) for reaction of any given acyl hydroperoxide with the iron(III) porphyrin are independent of [H$_3$O$^+$] from pH 2.2 to 6.7. It is concluded, since an increase in a_H of 3.7 × 10^4-fold (to a maximum [H$_3$O$^+$] = 6 × 10^{-3} M) does not influence k_{ly}, that the reactions of acyl hydroperoxides with the iron(III) porphyrin are not subject to either specific or general-acid catalysis. Linear free energy plots of log k_{ly} determined at pH 2.2 and 6.7 vs the pK_a of YOH species exhibit a marked break in slope ($-\beta_{lg}$). The $-\beta_{lg}$ values for acyl hydroperoxides [and Ph$_2$C(CN)OOH] are substantially greater (0.63 and 0.36 at pH 2.2 and 6.7, respectively) than the $-\beta_{lg}$ values for alkyl hydroperoxides (0.18 and 0.11 at pH 2.2 and 6.7, respectively). The marked difference in the $-\beta_{lg}$ values, when comparing acyl and alkyl hydroperoxides, is ascribed to a change in the rate-limiting step from heterolytic O–O bond breaking for acyl hydroperoxides to homolytic O–O bond breaking with alkyl hydroperoxides. Between pH 5 and 7 the formation of an iron(IV)–oxo porphyrin species is observed. Oxygen need not be present for the formation of the iron(IV)–oxo porphyrin species when the oxidant is one of the various acyl hydroperoxides. The second-order rate constants for the reaction of the various acyl hydroperoxides with (1)Fe^{IV}(OH)(X) at pH 6.7 have been determined. Since the reaction of acyl hydroperoxides with iron(III) porphyrins involves heterolytic O–O bond scission, the direct porphyrin product is at the compound I level of oxidation. The iron(IV) porphyrin species is proposed to be formed by reaction of remaining (1)Fe^{III}(H$_2$O)(X) with (+•1)-Fe^{IV}(O)(X). When the various alkyl hydroperoxides are oxidants, the presence of O$_2$ is required to observe the formation of iron(IV)–oxo porphyrin. The formation of iron(IV)–oxo porphyrin with alkyl hydroperoxides is due to the reaction of O$_2$ with (1)Fe^{II}(H$_2$O)$_2$. The latter may be trapped by CO. Finally, it is shown that (1)Fe^{III}(H$_2$O)(X) does not catalyze the epoxidation of 3-cyclohexene-1-carboxylic acid (at 1.0 M) when employing t-BuOOH as oxidant at pH 7.0.

We have determined the second-order rate constants (k_{ly}) for the oxidation reactions accompanying oxygen transfer from acyl and alkyl hydroperoxides (YOOH species) to metal(III) porphyrins with the (meso-tetraphenylporphinato)metal(III) chlorides (TPP)Cr^{III}(Cl),[1a,b] (TPP)Fe^{III}(Cl),[1a,c] (TPP)Mn^{III}(Cl),[1d] and (TPP)Co^{III}(Cl),[1e] as well as the imidazole (ImH) ligated (TPP)Mn^{III}(Cl)(ImH).[1f] In some instances [i.e., (TPP)Cr^{III}(Cl)], plots of log k_{ly} vs the pK_a of YOH are linear, with the points for acyl hydroperoxides and alkyl hydroperoxides fitting a single line. This information, and other evidence,[1,2] supports a heterolytic O–O bond cleavage in the oxidation of the metal(III) porphyrin when YOOH represents acyl or alkyl hydroperoxides. In other instances [i.e., (TPP)Fe^{III}(Cl)], a plot of log k_{ly} vs pK_a of YOH exhibits a break (at pH ~11), with acyl hydroperoxides and more acidic alkyl hydroperoxides exhibiting a greater dependence on the pK_a of YOH compared to the less acidic alkyl hydroperoxides. In such instances we proposed a change in the rate-limiting step from heterolytic to homolytic O–O bond breaking.

Results of studies of the dynamics of reactions in organic solvents can be misleading if the reactants possess dissociable protons. This is so since there is no reliable means of determining proton activity and the acid dissociation constants of starting

materials and intermediates in organic solvents. Thus, an investigation of the reaction of iron(III) porphyrin with various acyl and alkyl hydroperoxides at constant hydrogen ion activities in aqueous medium is of the utmost importance.

Our previous studies in aqueous medium have dealt with the mechanism of the reactions of H$_2$O$_2$ and t-BuOOH with the water-soluble and non-μ-oxo dimer forming (meso-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato)iron(III) hydrate [(1)-Fe^{III}(H$_2$O)(X), where X = HO$^-$ or H$_2$O]. From these we know that the reactions involve a number of critical peroxide–iron(III) porphyrin complexes in the rate of oxygen transfer.[3,4] The importance of each complex to the rate is dictated by the pH (2–13). In the present investigation details of the reaction of a series of alkyl and acyl hydroperoxides with (1)Fe^{III}(H$_2$O)(X) are enumerated.

Experimental Section

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hydroperoxide (Sigma) was used as received. *tert*-Butyl hydroperoxide (Aldrich) was obtained as a 70% aqueous solution and used as received. Phenylperacetic acid,[5] perhexanoic acid,[6] diphenylcyanomethyl hydroperoxide,[7] and carbomethoxydiphenylmethyl hydroperoxide[8] were prepared by using literature procedures. The "peroxo" contents of all acyl and alkyl hydroperoxide solutions were determined by iodometric analyses prior to use, as described elsewhere.[9]   2,4,6-Trimethylpyridine (Sigma, purified grade) was stirred for 24 h over KOH and then distilled from BaO under vacuum. Buffer solutions were prepared from reagent-grade chloroacetic acid (Aldrich and Matheson Collman Chemicals), and sodium phosphates (NaH_2PO_4, Na_2HPO_4) and were made free from heavy-metal impurities as described previously.[3] 4-(4'-Nitrobenzyl)-pyridine (Aldrich) was used as received. 3-Cyclohexene-1-carboxylic acid ($C_6H_9CO_2H$) was prepared by PDC oxidation of 1,2,3,6-tetrahydrobenzaldehyde (Aldrich) and purified by vacuum distillation. Methyl 3-cyclohexene-1-carboxylate ($C_6H_9CO_2CH_3$) [^{1}H NMR ($CDCl_3$) δ 1.619–1.669 (m, 1 H), 1.951–1.999 (m, 1 H), 2.019–2.104 (m, 2 H), 2.218–2.233 (m, 2 H), 2.510–2.570 (m, 1 H), 3.662 (s, 3 H), 5.654 (s, 2 H)] was prepared by reacting diazomethane with 3-cyclohexene-1-carboxylic acid in ether and purified by bulb-to-bulb distillation. Methyl 3,4-epoxycyclohexane-1-carboxylate[10] ($C_6H_9OCO_2CH_3$) [^{1}H NMR ($CDCl_3$) δ 1.360–1.428 (m), 1.542–1.634 (m), 1.708–1.777 (m), 1.856–1.984 (m), 2.073–2.265 (m), 2.463–2.518 (m), 3.109–3.130 (m), 3.200–3.216 (m), 3.639 (s), 3.643 (s)] was prepared by m-$ClC_6H_4CO_3H$ oxidation of $C_6H_9CO_2CH_3$ in ether and purified by column chromatography on silica gel with ether as the eluant followed by bulb-to-bulb distillation. The ^{1}H NMR spectral data for $C_6H_9OCO_2CH_3$ is consistent with the presence of two isomers, syn and anti, in an approximate ratio of 1:2, as was observed by Bellucci and co-workers.[10]

Instrumentation. Measurements of pH were carried out with a Radiometer Model pH M26 with a Metrohm electrode. UV–vis spectral measurements and kinetics were carried out in cell holders thermostated at 30 °C with a Perkin-Elmer Model 553 fast-scan spectrophotometer. A Hewlett-Packard 9825A computer, equipped with a 9864A digitizer and plotter, was employed for the analysis of pseudo-first-order kinetic traces. Rapid reactions were followed either with a Durrum-Gibson D-110 stopped-flow spectrophotometer or with a rapid-scan stopped-flow apparatus at 24 °C. These spectrophotometers were interfaced to Zenith computers equipped with OLIS (On-Line Instrument Systems, Inc., Jefferson, GA) data acquisition and processing software. GC analyses were performed on a Varian 3700 gas chromatograph [flame ionization detector, Varian WCOT capillary column (0.2-mm i.d., 25-m length, vitreous silica)] interfaced to a Hewlett-Packard 3392A integrator. GC response factors were calibrated with authentic samples. Injector and detector temperatures were maintained at 250 °C and the analyses performed at 75 °C (isothermal). The retention times are as follows: $C_6H_9CO_2CH_3$, 4.0 min; $C_6H_9OCO_2CH_3$, 10.5 and 12.2 min. ^{1}H NMR spectra were obtained by using a General Electric GN-500 (500-MHz) spectrometer referenced to residual $CHCl_3$ present in $CDCl_3$.
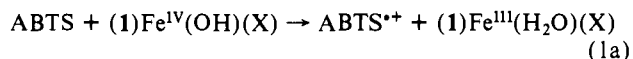
Kinetic Studies. Phosphate and chloroacetate buffer solutions were prepared by mixing known concentrations of Na_2HPO_4/NaH_2PO_4 and $ClCH_2CO_2H/HO^-$ to yield the desired pH values. 2,4,6-Trimethylpyridine/2,4,6-trimethylpyridine·HCl buffer was prepared by mixing a known amount of 2,4,6-trimethylpyridine with sufficient quantities of dilute HCl to yield the appropriate pH value.[11] Sodium nitrate was used to maintain the ionic strength at 0.22. Stock solutions of $(1)Fe^{III}$-$(H_2O)(X)$ were prepared in doubly distilled H_2O and stored in blackened glass containers at 3–5 °C. Slower alkyl hydroperoxide reactions were studied by mixing 50 μL of a methanolic solution of the corresponding alkyl hydroperoxide ($\sim 5.0 \times 10^{-3}$ M) with the buffered $(1)Fe^{III}$-$(H_2O)(X)$ solution containing ABTS. At pH 2.2, reactions of alkyl hydroperoxide with $(1)Fe^{III}(H_2O)(X)$ could not be followed under aerobic conditions due to the competing reaction of atmospheric O_2 with ABTS, which is catalyzed by $(1)Fe^{III}(H_2O)(X)$.[3a,4a] Therefore, alkyl hydroperoxide reactions at pH 2.2 were followed inside a nitrogen-filled glovebox. The pHs of the reaction mixtures were checked to be within ±0.05 pH unit before and after the completion of each kinetic run. Rapid acyl hydroperoxide reactions were followed by rapid-scan stopped-flow

spectrophotometry (under aerobic and anaerobic conditions) as well as by stopped-flow spectrophotometry (aerobic) by mixing buffered acyl hydroperoxide solutions of known concentrations and buffered solutions of $(1)Fe^{III}(H_2O)(X)$ with no ABTS present in the reaction mixture. Solubility problems for the organic acyl hydroperoxides in aqueous medium were successfully avoided by preparing a methanolic stock solution of acyl hydroperoxide and then diluting a small volume with the desired buffer solutions. The volume percentage of methanol was kept below 2%. The pseudo-first-order rate constants for the rapid reactions were determined by two methods: (i) from the analysis of absorbance vs time of the stopped-flow kinetic traces with a Zenith computer equipped with OLIS data acquisition and processing software and (ii) by reading the absorbance and time values of the rapid-scanned spectra and then fitting the data with either two-exponential or rise–fall software programs. Values of the second-order rate constants determined by both methods varied by no greater than 0.13 log unit.

Epoxidation Studies. At low concentrations of alkene, product analyses were carried out by GC employing authentic epoxide as standard. Reaction solutions were formulated to the following compositions: [*t*-BuOOH]$_i$ = 7×10^{-3} M, [$(1)Fe^{III}(H_2O)(X)$]$_i$ = 1.2×10^{-5} M, and [3-cyclohexene-1-carboxylic acid]$_i$ = 8.6×10^{-3} M. Solutions were maintained at pH 6.6 by phosphate buffer (0.05 M) and μ = 0.29 with $NaNO_3$. The course of the reaction was followed by monitoring the Soret maximum of $(1)Fe^{IV}(OH)(X)$ at 420 nm. When no further change was observed (appropriately 16 h) the pH was adjusted to $\sim$3 and the reaction solution immediately extracted 3× with 10 mL of ether. The ether fractions were combined, and a saturated ethereal solution of CH_2N_2 was added such that the resultant solution remained faintly yellow. The solution was dried over $MgSO_4$, the ether removed under vacuum, and the residue quantitatively transferred with CH_2Cl_2 to a 1.0-mL volumetric flask. No epoxide, or less than 0.5% based on the [*t*-BuOOH]$_i$, was detected by gas chromatography (GC detection limit for authentic methyl 3,4-epoxycyclohexane-1-carboxylate is $\sim 4 \times 10^{-4}$ M). A colorimetric assay for epoxide (vide infra) was employed when high concentrations of alkene were employed. Choice of such an assay was based on the engulfment of any small GC epoxide peak by the very large concentrations of alkene. Reaction solutions were formulated to the following compositions: [*t*-BuOOH]$_i$ = 7×10^{-3} M, [$(1)Fe^{III}(H_2O)(X)$]$_i$ = 1.0×10^{-5} M, and [3-cyclohexene-1-carboxylic acid]$_i$ = 1.0 M; and reactions were carried out at pH 7.0 and 11.5 (μ = 1.2). Blank reaction solutions were of the same composition sans the presence of iron(III) porphyrin. The reaction solutions and blank solutions were worked up in the same manner as the experiments conducted at lower alkene concentration. Aliquots (15–50 μL) of the residues were subjected to the colorimetric analyses described by Agarwal and co-workers.[12] The analytical procedure is based upon the formation of a bluish-purple adduct (λ_{max} = 580 nm, ϵ_{580} = 4.5×10^3 M^{-1} cm^{-1}) produced in the reaction of 4-(4'-nitrobenzyl)pyridine with methyl 3,4-epoxycyclohexane-1-carboxylate using acetone as solvent. At pH 7.0, under both aerobic and anaerobic conditions, *t*-BuOOH and sodium 3-cyclohexene-1-carboxylate produced a positive colorimetric assay corresponding to 13 ± 3% epoxide based upon [*t*-BuOOH]$_i$ and the average of five runs. ^{1}H NMR spectral examination of the extracted reaction mixtures were unamenable to epoxide detection due to the high concentration of alkene. At pH 7.0, the presence of $(1)Fe^{III}(H_2O)(X)$ in the reaction solutions did not provide an increase in the yield of epoxide (12 ± 3%; average of five runs). Based upon three reaction runs and three blank runs, at pH 11.5, there was a slight increase in epoxide yield in the presence of $(1)Fe^{III}(H_2O)(X)$ 15 ± 2% vs 11 ± 1% for the uncatalyzed reactions.

Results

The kinetics of the reactions of (*meso*-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato)iron(III) hydrate [$(1)Fe^{III}$-$(H_2O)(X)$; X = HO^- or H_2O] with m-$ClC_6H_4CO_3H$, p-$O_2NC_6H_4CO_3H$, $PhCH_2CO_3H$, n-$C_5H_{11}CO_3H$, Ph_2C-$(CO_2CH_3)OOH$, $Ph_2C(CN)OOH$, and $PhC(CH_3)_2OOH$ (YOOH species) have been studied in aqueous medium (μ = 0.22 with $NaNO_3$). Reactions of alkyl hydroperoxides with $(1)Fe^{III}$-$(H_2O)(X)$ were followed (30 °C) by trapping the intermediates, $(1)Fe^{IV}(OH)(X)$ and YO$^\bullet$, with 2,2'-azinobis(3-ethylbenzthiazolinesulfonic acid) (ABTS) (eq 1). An alternate to the

$$ABTS + (1)Fe^{IV}(OH)(X) \rightarrow ABTS^{\bullet +} + (1)Fe^{III}(H_2O)(X) \tag{1a}$$

$$ABTS + YO^\bullet \rightarrow ABTS^{\bullet +} + YO^- \tag{1b}$$

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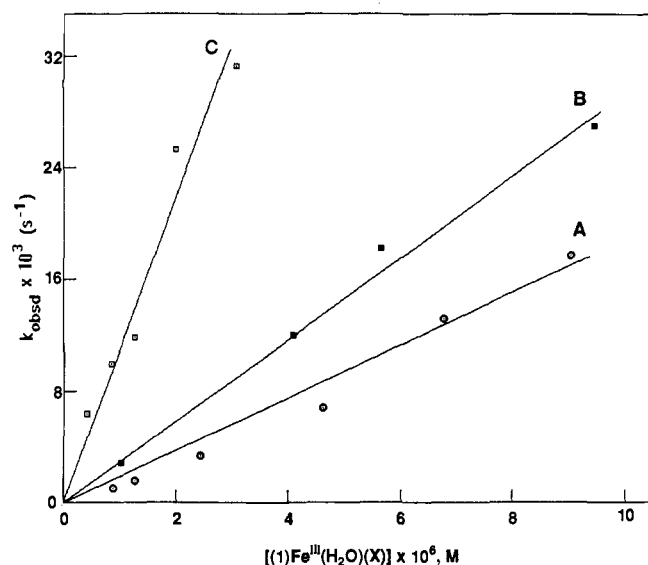
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Figure 1. Dependence of the pseudo-first-order rate constant (k_{obsd}) for the reaction of alkyl hydroperoxides with $(1)Fe^{III}(H_2O)(X)$ on the concentration of the latter species (pH 6.77 with Na_2HPO_4/NaH_2PO_4 buffer at 0.068 M, 30 °C, $\mu = 0.22$ $NaNO_3$). Line A, $PhC(CH_3)_2OOH$ (7.64 × 10^-5 M). Line B, $Ph_2C(CO_2CH_3)OOH$ (7.5 × 10^-5 M). Line C, $Ph_2C(CN)OOH$ (9.0 × 10^-5 M).

Table I. Dependence of k_{obsd} on $[ABTS]_i$ for the Reactions of $PhC(CH_3)_2OOH$ $[[alkyl-OOH]_i = 7.64 \times 10^{-5}$ M, $[(1)Fe^{III}(H_2O)(X)]_i = 4.6 \times 10^{-6}$ M] and $Ph_2C(CN)OOH$ $[[alkyl-OOH]_i = 9.3 \times 10^{-5}$ M, $[(1)Fe^{III}(H_2O)(X)]_i = 1.62 \times 10^{-6}$ M] at pH 6.77 and $\mu = 0.22$ $(NaNO_3)$

$[ABTS]_i$, M	k_{obsd}, s^{-1}	$[ABTS]_i$, M	k_{obsd}, s^{-1}
(a) With $PhC(CH_3)_2OOH$		(b) With $Ph_2C(CN)OOH$	
1.59 × 10^-3	6.90 × 10^-3	1.12 × 10^-3	2.20 × 10^-2
2.66 × 10^-3	6.92 × 10^-3	2.33 × 10^-3	2.06 × 10^-2
6.03 × 10^-3	7.75 × 10^-3	6.21 × 10^-3	1.60 × 10^-2
7.78 × 10^-3	7.80 × 10^-3	7.72 × 10^-3	1.62 × 10^-2
1.00 × 10^-2	6.92 × 10^-3	1.00 × 10^-2	1.60 × 10^-2

Table II. Values of k_{ly} for the Reaction of $(1)Fe^{III}(H_2O)(X)$ with the Alkyl Hydroperoxides at Two $[B_T]$ Values (30 °C, $\mu = 0.22$ $NaNO_3$)

alkyl-OOH	pH	$[B_T]$, M	k_{ly}, M^{-1} s^{-1}
$PhC(CH_3)_2OOH$	6.77	0.0680	1.50 × 10³
$PhC(CH_3)_2OOH$	6.77	0.0068	1.33 × 10³
$Ph_2C(CO_2CH_3)OOH$	6.77	0.0680	3.26 × 10³
$Ph_2C(CO_2CH_3)OOH$	6.77	0.0068	4.36 × 10³
$Ph_2C(CN)OOH$	6.77	0.0680	1.06 × 10⁴
$Ph_2C(CN)OOH$	6.77	0.0068	0.92 × 10⁴
$PhC(CH_3)_2OOH$	2.20	0.050	3.98 × 10¹
$PhC(CH_3)_2OOH$	2.20	0.005	2.50 × 10¹
$Ph_2C(CO_2CH_3)OOH$	2.20	0.050	5.00 × 10²
$Ph_2C(CO_2CH_3)OOH$	2.20	0.005	3.27 × 10²
$Ph_2C(CN)OOH$	2.20	0.050	5.51 × 10²
$Ph_2C(CN)OOH$	2.20	0.005	3.60 × 10²

formulation $(1)Fe^{IV}(OH)(X)$ would be $(1)Fe^{IV}(O)(H_2O)$, as proposed from studies in nonaqueous solvent.[1a,2,13] Reactions were carried out under the pseudo-first-order condition $[(1)Fe^{III}(H_2O)(X)]_i < [YOOH]_i \ll [ABTS]_i$ and followed by monitoring the appearance of ABTS$^{\bullet+}$ at 660 nm ($\epsilon_{max} = 1.2 \times 10^4$ M^{-1} cm^{-1}). Because acyl hydroperoxides oxidize ABTS with a significant rate constant, the latter could not be used as a trap when YOOH = RCO_3H. Acyl hydroperoxide reactions were carried out (24 °C) under pseudo-first-order conditions $([(1)Fe^{III}(H_2O)(X)]_i < [YOOH])$ in the absence of ABTS, and the pseudo-first-order rate constants were determined by monitoring the disappearance of the Soret maximum of $(1)Fe^{III}(H_2O)(X)$. Rate constants with acyl hydroperoxides were determined at a lower temperature (24 °C) than in the case of alkyl hydroperoxides (30 °C). This is admittedly unusual. The acyl hydroperoxide rate constants were of such magnitude that they could not be assuredly determined at the higher temperature. Since free energies of activation are compared (see Discussion), this is not a major consideration.

Dependence of the Pseudo-First-Order Rate Constant (k_{obsd}) for ABTS$^{\bullet+}$ Formation on $[(1)Fe^{III}(H_2O)(X)]$ in the Reaction of Alkyl Hydroperoxides with $(1)Fe^{III}(H_2O)(X)$. Values of k_{obsd} were determined over a 10-fold change in the concentration of $(1)Fe^{III}(H_2O)(X)$ (1.0 × 10^-6–1.0 × 10^-5 M) at constant pH values (6.77 and 2.20) and $[alkyl-OOH]_i = 7.5 \times 10^{-5}$ M. Values of k_{obsd} increase linearly as a function of $[(1)Fe^{III}(H_2O)(X)]$, as shown in the plots of k_{obsd} vs $[(1)Fe^{III}(H_2O)(X)]_i$ (at pH 6.77) in Figure 1 for $Ph_2C(CO_2CH_3)OOH$, $Ph_2C(CN)OOH$, and $PhC(CH_3)_2OOH$. Similar results were obtained upon plotting k_{obsd} vs $[(1)Fe^{III}(H_2O)(X)]_i$ at pH 2.20. Thus, the reactions of alkyl-OOH species are first order in $[(1)Fe^{III}(H_2O)(X)]$.

The dependence of k_{obsd} on the concentrations of $PhC(CH_3)_2OOH$ and $Ph_2C(CN)OOH$ was determined at constant $[(1)Fe^{III}(H_2O)(X)]_i$ [1.24 × 10^-6 M for $PhC(CH_3)_2OOH$ and 1.62 × 10^-6 M for $Ph_2C(CN)OOH$] and [ABTS] (1.0 × 10^-2 M) at pH 6.77. An independence of k_{obsd} on $[alkyl-OOH]_i$ was observed. Thus, the reaction is first order in the concentration of alkyl hydroperoxide. (For catalytic turnover reactions, values of k_{obsd} are independent of $[substrate]_i$ below saturation of catalyst.)[3,4a] Average values of k_{obsd} for $PhC(CH_3)_2OOH$ and $Ph_2C(CN)OOH$ at the given $[(1)Fe^{III}(H_2O)(X)]_i$ are (2.0 ± 0.4) × 10^-3 and (1.9 ± 0.5) × 10^-2 s^-1, respectively.

The dependence of k_{obsd} on the concentration of ABTS was determined (pH 6.77) at constant $[(1)Fe^{III}(H_2O)(X)]_i$ with $PhC(CH_3)_2OOH$ and $Ph_2C(CN)OOH$. Values of k_{obsd} (Table I) are independent, within experimental error, of [ABTS] over a 10-fold change in the latter's concentration. Therefore, reactions of alkyl-OOH with $(1)Fe^{III}(H_2O)(X)$ are zero order in [ABTS] and the rate law for the formation of ABTS$^{\bullet+}$ is given as follows:

$$v = k_{ly}[(1)Fe^{III}(H_2O)(X)][alkyl-OOH] \qquad (2)$$

and

$$k_{ly} = k_{obsd}/[(1)Fe^{III}(H_2O)(X)]$$

Buffer dilution experiments employing Na_2HPO_4/NaH_2PO_4 (pH 6.77) and $ClCH_2CO_2H/ClCH_2CO_2^-$ (pH 2.20) buffers were carried out for the alkyl hydroperoxide reactions. The apparent second-order rate constants (k_{ly}) for each alkyl hydroperoxide were determined, at two different total buffer concentrations ($[B_T]$), by plotting k_{obsd} vs $[(1)Fe^{III}(H_2O)(X)]_i$ (1.0 × 10^-6–1.0 × 10^-5 M). The results are provided in Table II. At pH 6.77, a 10-fold change in $[B_T]$ shows no change (within experimental error) in the values of k_{ly}, whereas at pH 2.20, the values of k_{ly} increase by only ~50% with a 10-fold increase in $[B_T]$. There is no apparent catalysis by oxyanion/oxyacid buffers for the reaction of alkyl hydroperoxides with $(1)Fe^{III}(H_2O)(X)$ at pH 6.77 and 2.20.

2,4,6-Trimethylpyridine/2,4,6-trimethylpyridine Hydrochloride Buffer Species Do Not Catalyze the Reaction of $(1)Fe^{III}(H_2O)(X)$ with $PhC(CH_3)_2OOH$ (pH 6.77) or $Ph_2C(CN)OOH$ (pH 6.38). The pseudo-first-order rate constants for the reaction of $PhC(CH_3)_2OOH$ were determined as a function of $[(1)Fe^{III}(H_2O)(X)]_i$ at $[B_T] = 5.0 \times 10^{-3}$ and 5.0 × 10^-2 M with ABTS as a trap (Figure 2). Inspection of Figure 2 shows that there is no catalysis for a 10-fold increase in $[B_T]$. The pseudo-first-order rate constants for the reaction of $Ph_2C(CN)OOH$ (1.26 × 10^-4 M) with $(1)Fe^{III}(H_2O)(X)$ (2.66 × 10^-6 M) were followed by observing the decrease in the Soret band with a 10-fold difference in $[B_T]$ (5.25 × 10^-3 and 5.25 × 10^-2 M). Average values (of eight kinetic runs for each $[B_T]$) for k_{obsd} were 2.07 ± 0.07 and 2.65 ± 0.16 s^-1, respectively. This demonstrates that there is no apparent catalysis by the nitrogen base/nitrogen acid buffer.

Reactions of the acyl hydroperoxides, m-$ClC_6H_4CO_3H$, $PhCH_2CO_3H$, p-$O_2NC_6H_4CO_3H$, and n-$C_5H_{11}CO_3H$ with (1)-

(13) See: Czernuszewicz, R. S.; Su, Y. O.; Stern, M. K.; Macor, K. A.; Kim, D.; Groves, J. T.; Spiro, T. S. *J. Am. Chem. Soc.* **1988,** *110,* 4158, and references therein.

Fe(III) Porphyrin Reactions with Hydroperoxides
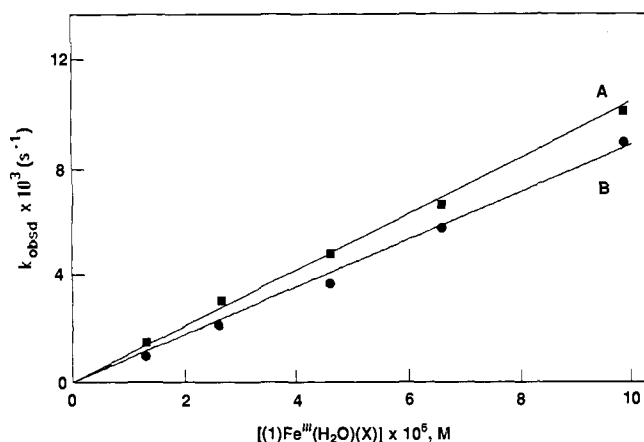
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Figure 2. Dependence of the pseudo-first-order rate constants (k_{obsd}) for the reaction of $PhC(CH_3)_2OOH$ (7.5×10^{-5} M) with $(1)Fe^{III}(H_2O)(X)$ on the concentration of the latter. Experiments have been carried out at pH 6.77 (30 °C, $\mu = 0.22$ NaNO$_3$) at two concentrations of 2,4,6-trimethylpyridine/2,4,6-trimethylpyridine hydrochloride buffer. Plot A, [B$_T$] = 0.05 M. Plot B, [B$_T$] = 0.005 M.
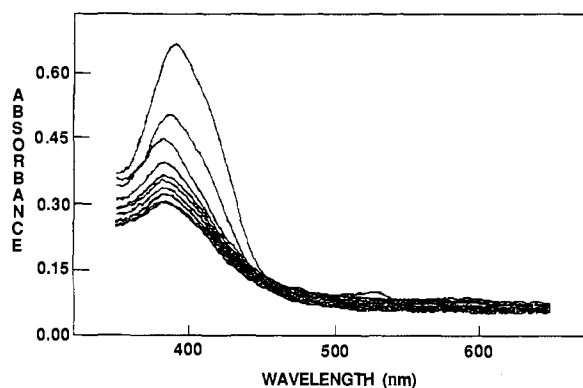

Figure 3. Rapid-scan stopped-flow spectral changes accompanying the reaction of $(1)Fe^{III}(H_2O)(X)$ (3.6×10^{-6} M) with m-ClC$_6$H$_4$CO$_3$H (5.2×10^{-5} M) at pH 2.20 showing the shift in the Soret maximum from 392 to 388 nm as the reaction proceeds (solutions buffered with ClCH$_2$CO$_2$H/ClCH$_2$CO$_2^-$ at [B$_T$] = 0.05 M, 24 °C, and $\mu = 0.22$ with NaNO$_3$). Ten scans were recorded in 2 s to monitor the observed spectral changes.

$Fe^{III}(H_2O)(X)$ were studied at pH 6.77 and 2.20 by stopped-flow and rapid-scan stopped-flow spectrophotometry. The spectral changes between 650 and 350 nm at pH 2.20 are shown in Figure 3 for the reaction of m-ClC$_6$H$_4$CO$_3$H (5.2×10^{-5} M) with (1)-Fe^{III}(H$_2$O)(X) (3.6×10^{-6} M). Examination of Figure 3 shows that the Soret maximum at 392 nm decreases and shifts to 388 nm as the reaction proceeds. Upon completion, there is seen an extensive degradation of the iron porphyrin. In order to determine the concentration of m-ClC$_6$H$_4$CO$_3$H consumed, the reaction time course was monitored spectrally (at 394 nm) until the absorbance reached a constant value [[m-ClC$_6$H$_4$CO$_3$H] = 3.0×10^{-5} M and [(1)Fe^{III}(H$_2$O)(X)] = 4.66×10^{-6} M]. Upon addition of ABTS (9.0×10^{-4} M), an 11% yield of ABTS$^{\bullet+}$ was observed (based on [m-ClC$_6$H$_4$CO$_3$H]$_i$). Thus, 6.3 equiv of m-ClC$_6$H$_4$CO$_3$H is turned over and 67% of the iron porphyrin is oxidatively decomposed. The shift in spectrum from 392 to 388 nm may signal the formation of a $(1)Fe^{IV}(OH)(X)$ species. If this is so, then the $(1)Fe^{IV}(OH)(X)$ species must be of lower extinction than the iron(III) species [i.e., $(1)Fe^{III}(H_2O)_2$] that is present at pH 2.20.

The formation of $(1)Fe^{IV}(OH)(X)$ ($\lambda_{max} = 421$ nm, $\epsilon_{max} = 1.3 \times 10^5$ M^{-1} cm^{-1}) has been observed,[4b] at pH 6.77, on reaction of m-ClC$_6$H$_4$CO$_3$H with $(1)Fe^{III}(H_2O)(X)$. In this study (pH 6.77), $(1)Fe^{IV}(OH)(X)$ has been observed to be formed on reaction of $(1)Fe^{III}(H_2O)(X)$ with PhCH$_2$CO$_3$H, p-O$_2$NC$_6$H$_4$CO$_3$H, and n-C$_5$H$_{11}$CO$_3$H. The kinetics of the acyl-OOH reactions with $(1)Fe^{III}(H_2O)(X)$ at pH 6.77 were followed under pseudo-first-order conditions with [acyl-OOH]$_i$ > [$(1)Fe^{III}(H_2O)(X)]_i$ (24 °C,
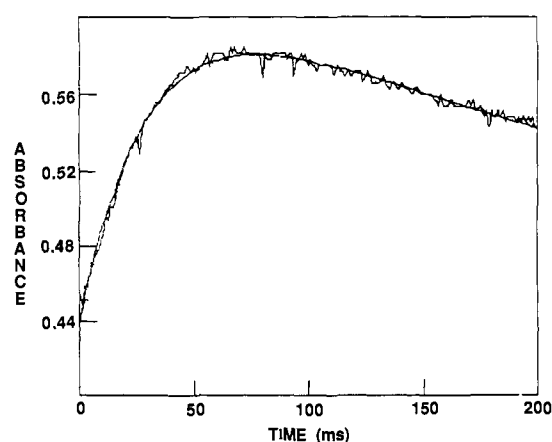
Figure 4. Plot of ΔA_{420} vs time for the reaction of m-ClC$_6$H$_4$CO$_3$H (1.95×10^{-5} M) with $(1)Fe^{III}(H_2O)(X)$ (2.8×10^{-6} M) (pH 6.77, Na$_2$HPO$_4$/NaH$_2$PO$_4$, [B$_T$] = 0.068 M, 24 °C, $\mu = 0.20$ with NaNO$_3$).
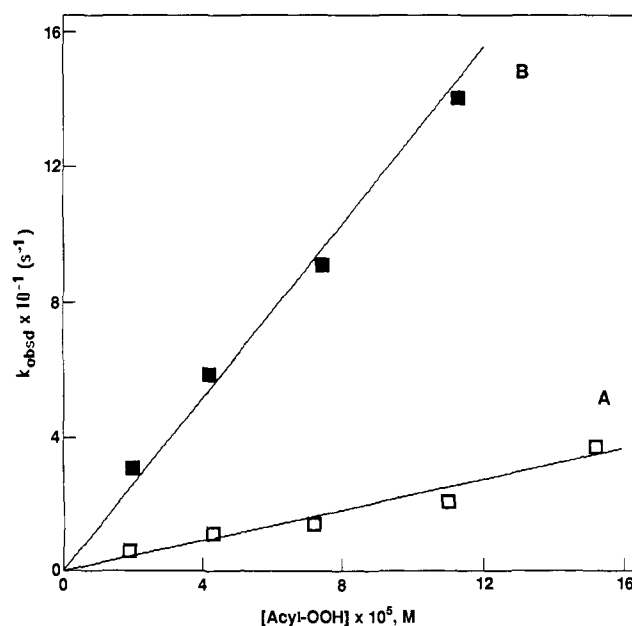

Figure 5. Pseudo-first-order rate constants (k_{obsd1}) for the build-up of $(1)Fe^{IV}(OH)(X)$ plotted vs acyl hydroperoxide concentration in the reaction of acyl hydroperoxides with $(1)Fe^{III}(H_2O)(X)$ ($\sim2.8 \times 10^{-6}$ M) (pH 6.77, Na$_2$HPO$_4$/NaH$_2$PO$_4$, [B$_T$] = 0.068 M, 24 °C, $\mu = 0.20$ with NaNO$_3$). The values of k_{obsd1} were determined from the first phase in the change of A_{420} with time. Line A refers to the reaction of PhCH$_2$CO$_3$H and line B corresponds to the reaction of m-ClC$_6$H$_4$CO$_3$H.

$\mu = 0.20$, NaNO$_3$) by monitoring the increase in absorbance at 420 nm due to the accumulation of $(1)Fe^{IV}(OH)(X)$ ($\lambda_{max} = 420$ nm, $\epsilon_{max} = 1.3 \times 10^5$ M^{-1} cm^{-1}). With time, the concentration of $(1)Fe^{IV}(OH)(X)$ (A_{420}) increases to a maximum value and then decreases (Figure 4), so that the reactions are biphasic. Kinetic traces were fitted to the equation for two sequential first-order reactions [formation (k_{obsd1}) and disappearance (k_{obsd2}) of A_{420} species]. Values of k_{obsd1} are linearly dependent upon [acyl-OOH]$_i$ (Figure 5). This is as expected for a second-order reaction without turnover. Thus, the formation of $(1)Fe^{IV}(OH)(X)$ is first order in [acyl-OOH]$_i$. From the slopes of Figure 5, the second-order rate constants (k_{1y}) are 1.2×10^6 and 1.5×10^5 M^{-1} s^{-1} for m-ClC$_6$H$_4$CO$_3$H and PhCH$_2$CO$_3$H, respectively. Because of lessened solubility, determination of the second-order rate constants for p-O$_2$NC$_6$H$_4$CO$_3$H (6.3×10^5 M^{-1} s^{-1}) and n-C$_5$H$_{11}$CO$_3$H (2.4×10^5 M^{-1} s^{-1}) were restricted to lower concentrations of the oxidants (<8 $\times$ 10^{-5} M).

The rate constants, k_{obsd2}, pertaining to the reactions of (1)-Fe^{IV}(OH)(X) at pH 6.77 with the various acyl-OOH species present in excess are given in Table III. The plots of k_{obsd2} vs [acyl-OOH] for each acyl hydroperoxide are reasonably linear
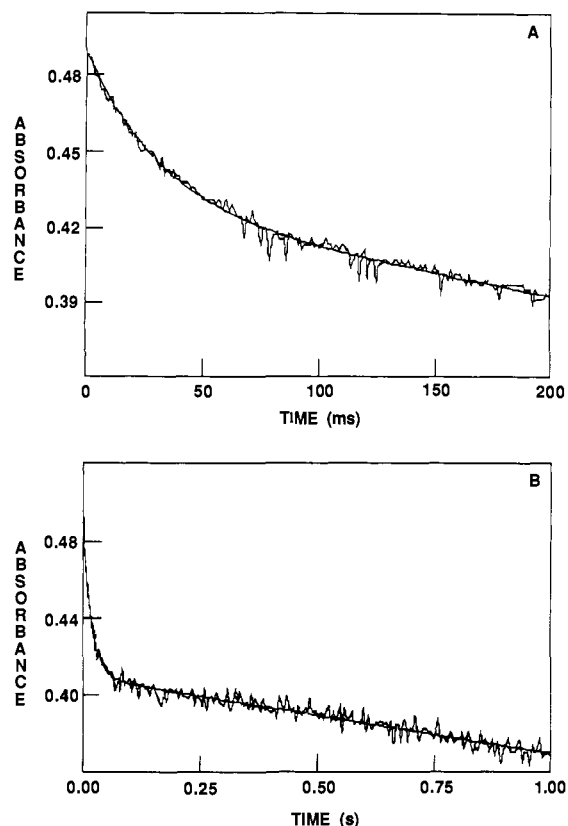
Figure 6. Plots of changes in absorbance vs time in the reaction of m-ClC$_6$H$_4$CO$_3$H (1.95 × 10^{-5} M) with (1)Fe^{III}(H$_2$O)(X) (2.8 × 10^{-6} M) (24 °C, μ = 0.20 with NaNO$_3$). Curve A corresponds to ΔA_{392} vs time at pH 2.20 (ClCH$_2$CO$_2$H/ClCH$_2$CO$_2^-$ at 0.05 M) and curve B represents ΔA_{410} vs time at 6.77 (Na$_2$HPO$_4$/NaH$_2$PO$_4$ at 0.068 M).

Table III. Values of k_{obsd2} for the Reaction of (1)Fe^{IV}(OH)(X) at pH 6.77 with the Various Acyl Hydroperoxides (24 °C, μ = 0.20, NaNO$_3$)

×10^5[PhCH$_2$CO$_3$H]$_i$, M	k_{obsd2}, s^{-1}	×10^5[n-C$_5$H$_{11}$CO$_3$H]$_i$, M	k_{obsd2}, s^{-1}
1.86	0.30	2.03	0.40
4.23	1.03	4.35	1.12
7.1	3.00	7.54	2.28
11	3.85	11.6	3.95
15.2	4.95	14.5	5.67

×10^5[p-O$_2$NC$_6$H$_4$CO$_3$H]$_i$, M	k_{obsd2}, s^{-1}	×10^5[m-ClC$_6$H$_4$CO$_3$H]$_i$, M	k_{obsd2}, s^{-1}
1.88	2.65	1.99	3.69
4.50	12.28	4.13	14.4
7.15	28.45	7.35	49.0
11.3	29.25		

with slopes equal to the bimolecular rate costants for the reaction of acyl hydroperoxides with (1)Fe^{IV}(OH)(X): PhCH$_2$CO$_3$H, 4.0 × 10^4 M^{-1} s^{-1}; n-C$_5$H$_{11}$CO$_3$H, 4.1 × 10^4 M^{-1} s^{-1}; p-O$_2$NC$_6$H$_4$CO$_3$H, 3.0 × 10^5 M^{-1} s^{-1}; and m-ClC$_6$H$_4$CO$_3$H, 5.1 × 10^5 M^{-1} s^{-1}.

The kinetics of the reaction of m-ClC$_6$H$_4$CO$_3$H, PhCH$_2$CO$_3$H, p-O$_2$NC$_6$H$_4$CO$_3$H, and n-C$_5$H$_{11}$CO$_3$H (pH 2.20 and 6.77) with (1)Fe^{III}(H$_2$O)(X) were also followed by monitoring the disappearance of (1)Fe^{III}(H$_2$O)(X) [at 410 nm (pH 6.77) and at 392 nm (pH 2.20)]. Reactions are biphasic and were fit to the appropriate equations for two sequential first-order reactions (as an example, see Figure 6). At pH 2.20, the rapid first phase of the reaction comprises 80% of the change in A_{392} and corresponds to the oxidation of (1)Fe^{III}(H$_2$O)(X) to a higher valent iron–oxo species while the remaining 20% change in absorbance is due to the reaction of acyl-OOH with the reactive higher valent iron–oxo species. At pH 6.77, the biphasic nature of the kinetic traces is due in part to the partial buildup of the intermediate (1)Fe^{IV}-(OH)(X) species. From the pseudo-first-order rate constants for the first phase of reaction (k_{obsd1}), the second-order rate constants
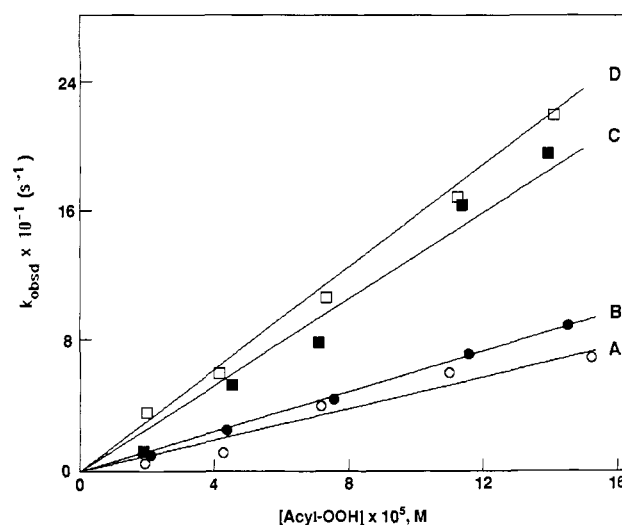

Figure 7. Pseudo-first-order rate constants (k_{obsd}) for the disappearance of (1)Fe^{III}(H$_2$O)(X) plotted vs acyl hydroperoxide concentration in the reaction of acyl hydroperoxides with (1)Fe^{III}(H$_2$O)(X) (~2.8 × 10^{-6} M) (pH 6.77, Na$_2$HPO$_4$/NaH$_2$PO$_4$, [B$_T$] = 0.068 M, 24 °C, μ = 0.20 with NaNO$_3$). The values of k_{obsd} were determined from the first phase in the decrease of A_{410} with time. Line A is for the reaction of PhCH$_2$CO$_3$H, line B is for the reaction of n-C$_5$H$_{11}$CO$_3$H, line C corresponds to the reaction of p-O$_2$NC$_6$H$_4$CO$_3$H, and line D represents the reaction of m-ClC$_6$H$_4$CO$_3$H.

(k_{ly}) for the reaction of (1)Fe^{III}(H$_2$O)(X) with acyl-OOH compounds may be obtained. Plots of k_{obsd1} vs [acyl-OOH]$_i$ for PhCH$_2$CO$_3$H, n-C$_5$H$_{11}$CO$_3$H, p-O$_2$NC$_6$H$_4$CO$_3$H, and m-ClC$_6$H$_4$CO$_3$H are given in Figure 7, and from their slopes, the bimolecular rate constants (k_{ly}) (at pH 6.77) were calculated. The second-order rate constants are as follows: PhCH$_2$CO$_3$H, 4.9 × 10^5 M^{-1} s^{-1}; n-C$_5$H$_{11}$CO$_3$H, 6.4 × 10^5 M^{-1} s^{-1}; p-O$_2$NC$_6$H$_4$CO$_3$H, 1.4 × 10^6 M^{-1} s^{-1}; and m-ClC$_6$H$_4$CO$_3$H, 1.6 × 10^6 M^{-1} s^{-1}. From these results it is seen that the values of k_{ly} determined by following the formation of (1)Fe^{IV}(OH)(X) at 420 nm are comparable to k_{ly} values determined by following the disappearance of (1)-Fe^{III}(H$_2$O)(X) at 410 nm. The second-order rate constants for the reactions with acyl hydroperoxides were also determined at pH 2.20 by following the disappearance of (1)Fe^{III}(H$_2$O)(X): PhCH$_2$CO$_3$H, 4.0 × 10^5 M^{-1} s^{-1}; n-C$_5$H$_{11}$CO$_3$H, 4.7 × 10^5 M^{-1} s^{-1}; p-O$_2$NC$_5$H$_4$CO$_3$H, 1.4 × 10^6 M^{-1} s^{-1}; and m-ClC$_6$H$_4$CO$_3$H, 1.8 × 10^6 M^{-1} s^{-1}. The rate law for the reactions of acyl hydroperoxide with (1)Fe^{III}(H$_2$O)(X) is written as in eq 3.

$$v = k_{ly}[(1)Fe^{III}(H_2O)(X)][acyl\text{-}OOH]$$

and

$$k_{ly} = k_{obsd}/[acyl\text{-}OOH] \qquad (3)$$

Discussion

The second-order rate constants for the reaction of (*meso*-tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphinato)iron(III) hydrate ((1)Fe^{III}(H$_2$O)(X)) with YOOH species [m-ClC$_6$H$_4$CO$_3$H, p-O$_2$NC$_6$H$_4$CO$_3$H, PhCH$_2$CO$_3$H, n-C$_5$H$_{11}$CO$_3$H, Ph$_2$C(CN)OOH, Ph$_2$C(CO$_2$CH$_3$)OOH and PhC(CH$_3$)$_2$OOH] were determined in aqueous medium at pH 2.20 and 6.77. Reactions with alkyl hydroperoxides were monitored [under pseudo-first-order conditions [(1)Fe^{III}(H$_2$O)(X)]$_i$ < [alkyl-OOH]$_i$] by employing a large excess of ABTS as a trapping agent for the reactive iron(IV)–oxo porphyrin and YO$^•$ intermediates. [The iron(IV)–oxo porphyrin may be written as (1)Fe^{IV}(OH)(X) or (1)Fe^{IV}(O)(X); exact ligation by oxygen is unknown in water.] In the case of the acyl hydroperoxides, reactions were studied in the absence of ABTS by following the disappearance of (1)-Fe^{III}(H$_2$O)(X) under the pseudo-first-order conditions of [(1)-Fe^{III}(H$_2$O)(X)]$_i$ < [acyl-OOH]$_i$. At pH 6.77, the rate of disappearance of (1)Fe^{III}(H$_2$O)(X) is equal to the rate of appearance of what has been established previously[4b] to be a (1)Fe^{IV}(OH)(X) intermediate and the pseudo-first-order rate constant for the
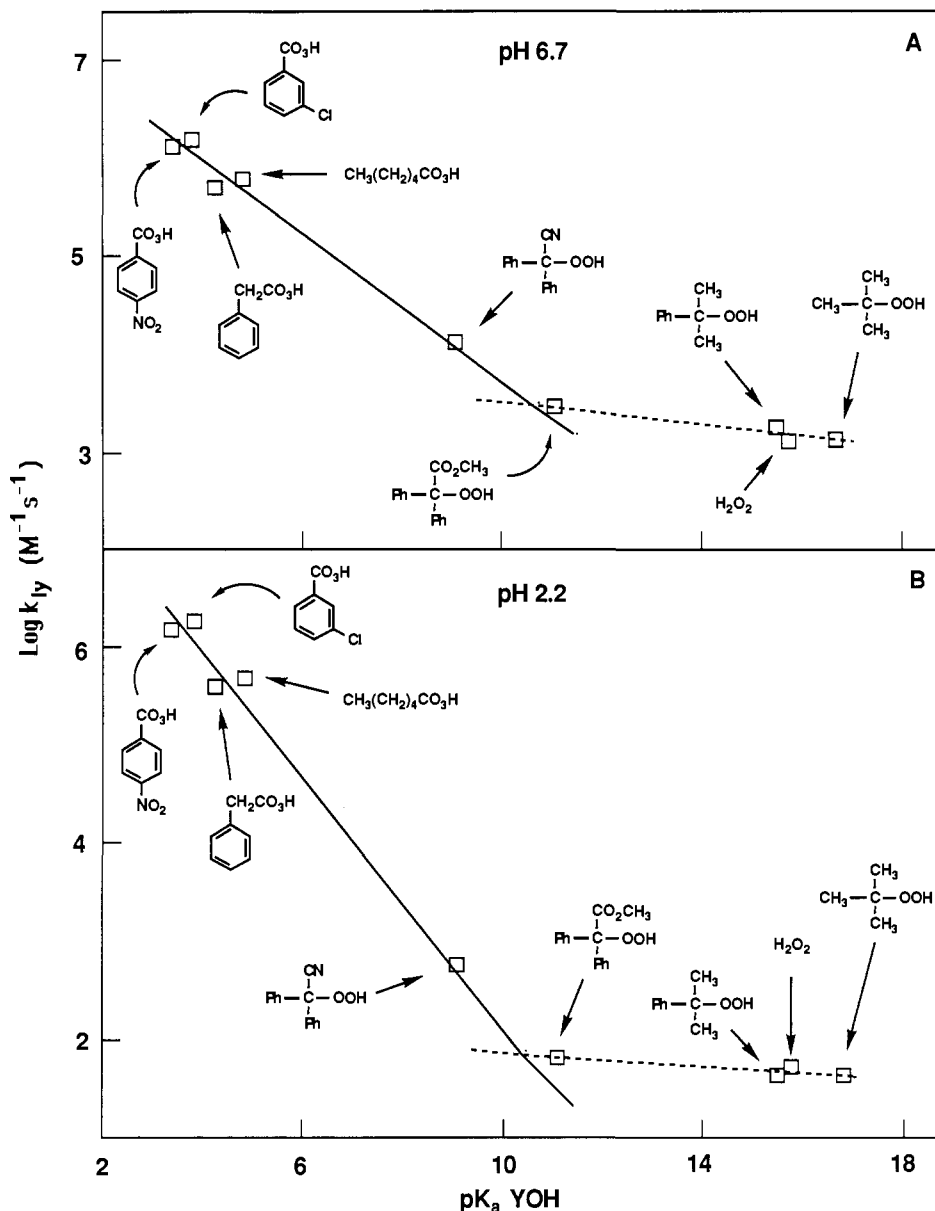
Figure 8. Plots of log of the second-order rate constants for the reaction of acyl and alkyl hydroperoxides (YOOH) with $(1)Fe^{III}(H_2O)(X)$ vs the pK_a of the putative leaving groups (YOH). Part A corresponds to the values of k_{ly} obtained at pH 6.7, while B represents the values of k_{ly} determined at pH 2.2.
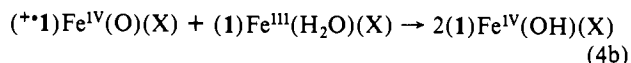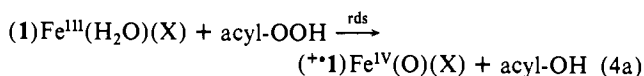
disappearance of $(1)Fe^{IV}(OH)(X)$ shows a linear dependence on $[acyl\text{-}OOH]_i$. In the course of these reactions, the porphyrin is extensively oxidatively decomposed.

The Role of General Catalysis in the Reaction of Alkyl Hydroperoxides and Hydrogen Peroxide with $(1)Fe^{III}(X)_2$ Species. We have previously shown that the reactions of t-BuOOH with $(1)Fe^{III}(H_2O)(X)$ are not subject to general-acid–base catalysis by oxyanion/oxyacid buffers.[4] In the present study, it is established that general-acid–base catalysis by oxyanion/oxyacid buffers is not seen in the reactions of $Ph_2C(CN)OOH$, Ph_2C-$(CO_2CH_3)OOH$, and $PhC(CH_3)_2OOH$ with $(1)Fe^{III}(H_2O)(X)$. Also, the second-order rate constants (k_{ly}) for reactions of PhC-$(CH_3)_2OOH$ and $Ph_2C(CN)OOH$ with $(1)Fe^{III}(H_2O)(X)$ are independent of the concentrations of the nitrogen base buffer 2,4,6-trimethylpyridine/2,4,6-trimethylpyridine·H^+. Independence of k_{ly} on [2,4,6-trimethylpyridine/2,4,6-trimethylpyridine·H^+] was previously shown with t-BuOOH.[4] Thus, for the reactions in water of the three alkyl hydroperoxides investigated with $(1)Fe^{III}$-$(H_2O)(X)$, general-acid and general-base catalysis is not involved. The reaction of H_2O_2 with $(1)Fe^{III}(H_2O)(X)$ is not subject to general calalysis with oxyanion/oxyacid buffers but the reaction is catalyzed by 2,4,6-trimethylpyridine/2,4,6-trimethylpyridine-

$\cdot H^+$.[3] Hydrogen peroxide appears as a special case, and further investigation is in progress.

Observation of the Formation of $(1)Fe^{II}(X)_2$ and $(1)Fe^{IV}$-$(OH)(X)$ Species. A $(1)Fe^{IV}(OH)(X)$ species has been observed on reaction of t-BuOOH and $PhC(CH_3)_2OOH$ with $(1)Fe^{III}$-$(H_2O)(X)$. Its formation requires the presence of O_2. In the absence of O_2, a $(1)Fe^{II}(X)_2$ species has been shown to be present as an intermediate.[4b] The $(1)Fe^{IV}(OH)(X)$ was identified by its spectroelectrochemical synthesis and comparison of its absorption spectrum to the authentic species as well as by titration with ABTS, whereas the $(1)Fe^{II}(X)_2$ species was identified spectrally after being trapped by carbon monoxide. Under the conditions of these experiments (water, 30 °C) formation of $(1)Fe^{IV}(OH)(X)$ occurs on reaction of O_2 with $(1)Fe^{II}(X)_2$. In contrast, the formation of $(1)Fe^{IV}(OH)(X)$ occurs in the absence of O_2 on reaction of $(1)Fe^{III}(H_2O)(X)$ with m-$ClC_6H_4CO_3H$.[4b] In the present study, $(1)Fe^{IV}(OH)(X)$ was also observed to be formed upon reaction of $(1)Fe^{III}(H_2O)(X)$ with $PhCH_2CO_3H$, n-$C_5H_{11}CO_3H$, and p-$O_2NC_6H_4CO_3H$ in the absence of O_2. A suitable explanation is that the acyl-OOH oxidizes $(1)Fe^{III}(H_2O)(X)$ while undergoing O–O bond heterolysis to provide $(^{+\bullet}1)Fe^{IV}(O)(X)$, which undergoes a comproportionation reaction with remaining $(1)Fe^{III}$-

$(H_2O)(X)$ (eq 4).[4b] The reactions of acyl hydroperoxides with

$$(1)Fe^{III}(H_2O)(X) + acyl\text{-}OOH \xrightarrow{rds}$$
$$(^{+\cdot}1)Fe^{IV}(O)(X) + acyl\text{-}OH \quad (4a)$$

$$(^{+\cdot}1)Fe^{IV}(O)(X) + (1)Fe^{III}(H_2O)(X) \rightarrow 2(1)Fe^{IV}(OH)(X)$$
$$(4b)$$

iron(III), manganese(III), chromium(III), and cobalt(III) *meso*-tetraphenylporphinato salts involve heterolytic O–O bond scission, as shown by use of $PhCH_2CO_3H$ accompanied by high recovery of phenylacetic acid.[1,2] An expectation of a homolytic reaction would be the recovery of products of $PhCH_2^\cdot$ (as bibenzyl[14,15]) due to the immediate decarboxylation of the intermediate $PhCH_2CO_2^\cdot$.

Comproportionation of metal(V)–oxo and metal(III) species (as in eq 4b) has been observed in the course of the reactions of acyl hydroperoxides with (*meso*-tetraphenylporphinato)chromium(III) chloride,[1a] in the reactions of (*meso*-tetrakis(substituted phenyl)porphinato)chromium(V)–oxo with alkenes,[16] and in the reactions of (*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato)-manganese(III) with hypochlorite.[17] At pH 6.77, the values of the apparent second-order rate constant for the formation of $(1)Fe^{IV}(OH)(X)$ agree favorably with k_{ly} for the disappearance of $(1)Fe^{III}(H_2O)(X)$. This shows that the minimal bimolecular rate constant for the comproportionation reaction of $(^{+\cdot}1)Fe^{IV}$-$(O)(X)$ and $(1)Fe^{III}(H_2O)(X)$ (eq 4b) to yield $2(1)Fe^{IV}(OH)(X)$ must be $>2.0 \times 10^6$ M^{-1} s^{-1} (the k_{ly} value determined with m-$ClC_6H_4CO_3H$). This is the first instance for which the bimolecular rate constant of eq 4b could be well approximated.

Epoxide was not formed (pH 7.0) on addition of sodium 3-cyclohexene-1-carboxylate (to 1.0 M) (see Experimental Section) to reaction solutions containing $[alkene]_i:[t\text{-}BuOOH]_i:[(1)Fe^{III}$-$(H_2O)(X)]_i = 860{-}10\,000{:}700{:}1$. At pH 11.5, a ~4% yield of epoxide could be detected. These results show that the $(1)Fe^{IV}$-$(OH)(X)$ species is not a useful epoxidation reagent and that $(^{+\cdot}1)Fe^{IV}(O)(X)$ is not formed with t-BuOOH at a concentration sufficient to react with the alkene (1.0 M). These observations are in accord with our finding that oxygen transfer from alkyl hydroperoxides is accompanied by homolytic cleavage of the peroxide O–O bond.
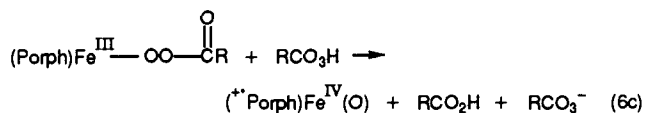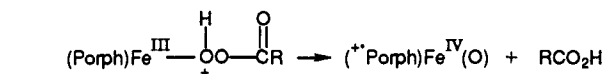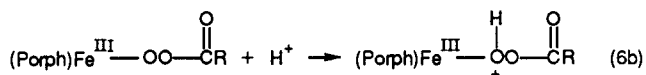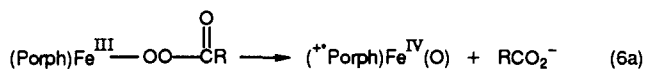
Stability of Higher Valent Iron–Oxo Porphyrin Species in the Presence of Acyl Hydroperoxides. With acyl hydroperoxides at pH 2.20, rapid-scan stopped-flow spectrophotometry reveals (Figure 3) a shift in the Soret maximum from 392 to 388 nm. This hypsochromic shift in the Soret may be due to a higher valent iron–oxo species; however, $(1)Fe^{IV}(OH)(X)$ does not accumulate, as observed at pH 6.77. This is due to the rate (eq 5) of disap-

$$(1)Fe^{IV}(OH)(X) + acyl\text{-}OOH \rightarrow catalyst\ degradation \quad (5)$$
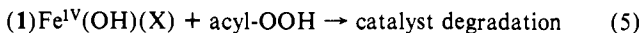
pearance of iron(IV)–oxo species, by reaction with remaining acyl hydroperoxide, exceeding the rate of formation of iron(IV)–oxo species. The second-order rate constants for the degradation of the iron porphyrin (pH 6.77) by reaction of acyl hydroperoxides with intermediate $(1)Fe^{IV}(OH)(X)$, calculated by use of the pseudo-first-order rate constants for disappearance of $(1)Fe^{IV}$-$(OH)(X)$ (k_{obsd2}) on reaction of $(1)Fe^{III}(H_2O)(X)$ with the acyl hydroperoxides, are between 4.0×10^4 and 5.0×10^5 M^{-1} s^{-1}. The iron(IV)–oxo intermediate species is observable only between pH 5 and 7.[4] Its relative stability in this pH range, compared to pH 2.20, must be due to the rate of disappearance of $(1)Fe^{IV}(OH)(X)$ [i.e., by reaction with the acyl hydroperoxide (eq 5)] being less than the rate for its formation [i.e., reaction of acyl hydroperoxide with $(1)Fe^{III}(H_2O)(X)$ (eq 4a)]. The structures of the iron-

(IV)–oxo porphyrin species are likely different at pH 2.2 vs pH 5–7. This structural difference could involve ionization of a ligated water molecule [possible structures being $(1)Fe^{IV}(OH)(OH)$ (pH 6.77) and $(1)Fe^{IV}(OH)(H_2O)$ (pH 2.20)]. It is known that addition of hydroxide ion or methoxide ion stabilizes the higher valent iron(IV)–oxo species in CH_2Cl_2 solvent[18] and manganese(IV)–oxo species in aqueous medium.[11]

General-Acid Catalysis of the Reaction of $(1)Fe^{III}(H_2O)(X)$ with Acyl Hydroperoxides. Groves et al.[19] observed a potentiation of the rate for the reaction of m-$ClC_6H_4CO_3H$ with $((CH_3)_{12}TP$-$P)Fe^{III}(Cl)$ in CH_2Cl_2 on addition of excess m-$ClC_6H_4CO_3H$. Arguments were presented which support a specific acid catalysis rather than general-acid catalysis. In the present study with acyl hydroperoxides, in aqueous solution, there is an independence of the apparent second-order rate constants (k_{ly}) on $[H_3O^+]$ (see Results). This lack of dependence of rate upon $[H_3O^+]$ rules out both specific and general-acid catalysis. Studies by Groves were carried out in dry aprotic solvents such that the generation of a carboxyl anion leaving group would be disfavored (eq 6a).

$$(Porph)Fe^{III}\text{—}OO\overset{O}{\overset{\|}{\text{—}C}}R \longrightarrow (^{+\cdot}Porph)Fe^{IV}(O) + RCO_2^- \quad (6a)$$

$$(Porph)Fe^{III}\text{—}OO\overset{O}{\overset{\|}{\text{—}C}}R + H^+ \longrightarrow (Porph)Fe^{III}\text{—}\overset{H}{\underset{+}{O}}O\overset{O}{\overset{\|}{\text{—}C}}R \quad (6b)$$

$$(Porph)Fe^{III}\text{—}\overset{H}{\underset{+}{O}}O\overset{O}{\overset{\|}{\text{—}C}}R \longrightarrow (^{+\cdot}Porph)Fe^{IV}(O) + RCO_2H$$

$$(Porph)Fe^{III}\text{—}OO\overset{O}{\overset{\|}{\text{—}C}}R + RCO_3H \longrightarrow$$
$$(^{+\cdot}Porph)Fe^{IV}(O) + RCO_2H + RCO_3^- \quad (6c)$$

Specific acid catalysis would result in the formation of an undissociated carboxylic acid (eq 6b). In such a system, general-acid catalysis by excess acyl hydroperoxide would not be expected since such a process would produce the even less stable acyl peroxide anion (eq 6c).

A lack of sensitivity in k_{ly} to a 3.7×10^4-fold change in $[H_3O^+]$ may be attributed to the following: (i) rates for reaction of $(1)Fe^{III}(X)(RCO_3H)$ and $(1)Fe^{III}(X)(RCO_3^-)$ are comparable; (ii) the acid dissociation of $(1)Fe^{III}(X)(RCO_3H)$ is associated with a $pK_a < 1.0$; or (iii) the pK_a of $(1)Fe^{III}(X)(RCO_3H)$ is >8.0. The alternative (iii) may be discarded. The solution to this problem is currently under investigation. With alkyl hydroperoxides, increasing the pH from 2 to 7 is accompanied by an increase in k_{ly} [for t-BuOOH and $PhC(CH_3)_2OOH$, an increase in k_{ly} of 22- and 33-fold, respectively]. This increase in k_{ly} with increasing pH has been suggested to be associated with the acid dissociation of eq 7.[4,20]

$$(1)Fe^{III}(H_2O)(YOOH) \underset{}{\overset{K_a}{\rightleftharpoons}} (1)Fe^{III}(H_2O)(YOO^-) + H^+ \quad (7)$$
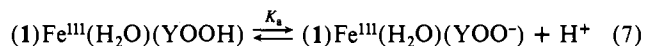
Linear Free Energy Relationships. The log k_{ly} vs pH profile for the reaction of t-BuOOH with $(1)Fe^{III}(H_2O)(X)$ exhibits a pH-insensitive plateau at low pH.[4] With increase in pH toward pH 7 the value of log k_{ly} reaches a maximal value, decreases, and then rises to a high plateau at high pH.[4] The second-order rate constants for the reaction of a series of YOOH compounds with $(1)Fe^{III}(H_2O)(X)$ were determined at the lower plateau (pH 2.2) and at the maximal value near neutrality (pH 6.7). At these pH values the reactive species with t-BuOOH are $(1)Fe^{III}(H_2O)(t$-$BuOOH)$ and $(1)Fe^{III}(H_2O)(t$-$BuOO^-)$, respectively. The plots of the log k_{ly} vs the pK_a of the leaving group (YOH), for the different acyl hydroperoxides and alkyl hydroperoxides (pH 2.20 and 6.77), are given in Figure 8 (A and B). At pH 2.20, the best

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line that correlates the experimental points for the acyl hydroperoxides and the more acidic alkyl hydroperoxides has a slope (β_{lg}) equal to -0.63, whereas the less acidic alkyl hydroperoxides form a separate series correlated by a best line of slope (β_{lg}) equal to -0.18. A similar behavior is seen for the linear free energy relationship at pH 6.77. In this case, β_{lg} for the acyl hydroperoxides and more acidic alkyl hydroperoxides is -0.36 and the corresponding β_{lg} value for the less acidic alkyl hydroperoxides is -0.11. These observations show that there is a break in the linear free energy plots. From a previous study in methanol the value of β_{lg} obtained for the reaction of $(TPP)Fe^{III}(Cl)$ with acyl hydroperoxides and the more acidic alkyl hydroperoxides is -0.36,

whereas with less acidic alkyl hydroperoxides the value of β_{lg} is -0.15.[1a,c] The agreement in the values of β_{lg} for the reaction of acyl hydroperoxides and more acidic alkyl hydroperoxides with $(TPP)Fe^{III}(Cl)$ in methanol solvent and with $(1)Fe^{III}(H_2O)(X)$ in H_2O at pH 6.77 (-0.36 vs -0.36) and the similarity in β_{lg} for the less acidic alkyl hydroperoxides (-0.11 vs -0.15) establish that our observations in methanol, in which the pH of the medium could not be accurately maintained, are valid.
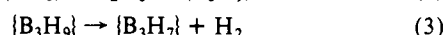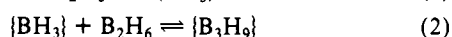
Communications to the Editor

Identity of the Rate-Determining Step in the Gas-Phase Thermolysis of Diborane: A Reinvestigation of the Deuterium Kinetic Isotope Effect

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The gas-phase thermolysis of diborane is known to be homogeneous in its initial stages and to follow $^3/_2$-order kinetics over a wide range of temperature and pressure.[1-3] This suggests that a triborane species is involved in the rate-determining step, and the currently favored mechanism involves a three-step process:[3-5]

$$B_2H_6 \rightleftharpoons 2\{BH_3\} \tag{1}$$

$$\{BH_3\} + B_2H_6 \rightleftharpoons \{B_3H_9\} \tag{2}$$

$$\{B_3H_9\} \rightarrow \{B_3H_7\} + H_2 \tag{3}$$

A triborane species has been generated by reaction of $\{BH_3\}$ with B_2H_6 in a fast-flow system and detected mass spectrometrically, but it was not possible to determine the number of hydrogen atoms in the species.[6]

Cogent arguments have been advanced to suggest that step 3 is the rate-determining step,[3,4] but a very recent high-level computational study employing many-body perturbation theory and the coupled-cluster approximation implies that it is the *formation* of $\{B_3H_9\}$ (step 2) rather than its decomposition (step 3) that is rate-determining.[7] The calculations also indicate that the $\{B_3H_9\}$ formed in step 2 carries about 80 kJ mol^{-1} of excess internal energy, suggesting that step 3 might occur so rapidly that for all practical purposes the formation of $\{B_3H_7\}$ might best be represented by the direct reaction:

$$\{BH_3\} + B_2H_6 \rightarrow \{B_3H_7\} + H_2 \tag{4}$$
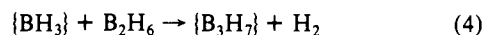
This possibility, which had been considered earlier but tentatively dismissed,[3] is easier to reconcile with the qualitative observation that added H_2 not only inhibits the rate of decomposition of B_2H_6[1] but also alters the product distribution in favor of volatile boranes;[8]

our own quantitative studies with Dr. M. D. Attwood[5,9] show that the initial rate of decomposition of B_2H_6 at 3.5 mmHg and 150 °C is decreased by a factor of 3.4 in the presence of a 14-fold excess of H_2.

The computations[7] also addressed the question of the relative rates of decomposition of B_2H_6 and B_2D_6 and found that, at 127 °C, the ratio of the rate constants (k_H/k_D) was 1.73 if step 2 were rate-determining and 2.4 if the rate-determining step were step 3; unfortunately the only experimental determination of this ratio (which was based on the relative rates of production of H_2 and D_2 at 88 °C)[3] gave a value of 5.0, which is compatible with neither of the computed values.

In an attempt to resolve these difficulties, we decided to undertake a careful experimental reinvestigation of the relative rates of decomposition of B_2H_6 and B_2D_6 using a mass spectrometric technique to monitor the initial stages of the reaction. We chose to monitor the rate of consumption of diborane rather than the rate of production of hydrogen since this was a more direct measure to compare with the calculated rates. The reactions were carried out at 147 °C in preconditioned spherical Pyrex bulbs (volume ca. 1 dm^3) with initial pressures of diborane about 3.5 mmHg; helium, argon, and krypton at partial pressures of 100, 1.0, and 1.0 mmHg, respectively, were also present as calibrants, etc., as previously described.[10,11] Initial rates were obtained by the tangent method from plots of diborane pressure vs time for 14 separate runs with B_2H_6 and 10 runs with B_2D_6: these yielded values for the $^3/_2$-order rate constants $k_H = (4.55 \pm 0.89) \times 10^{-4}$ and $k_D = (1.77 \pm 0.28) \times 10^{-4}$ mol$^{-1/2}$ m$^{3/2}$ s^{-1}, respectively. The value of the ratio k_H/k_D is therefore 2.57 ± 0.65, which is clearly more consistent with the computed values[7] than with the early experimental value based on the rates of production of H_2 and D_2.[3] The new experimental value is closer to the computed value of 2.4 assuming step 3 as rate-determining than to the value of 1.73 for step 2 as rate-limiting, but in view of the expected uncertainties in the theoretical values, it is probably more appropriate to suggest that both of the computed values are in adequate agreement with the new experimental value.[12] We note parenthetically that the computed overall activation energy for the decomposition of diborane is 134 kJ mol^{-1} if step 2 is rate-determining but only 92 kJ mol^{-1} if step 3 is rate-determining;[7] our own most recent experimental redetermination of this quantiy

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