

$\varphi$  and  $\langle\omega^2\rangle$  values obtained for the three crystal modifications at the various temperatures. The curve for **W1** represents the average over the two independent molecules. The quantity  $\langle\omega^2\rangle^{1/2}$  corresponds to the half-width of a parabolic energy well at the height  $RT/2$  above its minimum.<sup>16</sup> The relative displacements of the three curves along the energy coordinate depend on the temperature, **Y1** being the most stable at room temperature and **W1** the most stable above about 375 K, as shown in Figure 2. The **Y1** and **LY1** curves are drawn at the same height since the phase transitions from **Y1** to **LY1** and from **LY1** to **Y1** have both been observed at about 375 K. The dashed curves connect the experimental energy wells and may be taken to portray in an approximate way the energy dependence on  $\varphi$  at a defect in the crystal and in a still more approximate way the energy profiles for the phase transformation.<sup>17</sup> At the temperature corresponding to the transformation of **Y1** to **W1** (380–410 K)<sup>5</sup> the extrapolated value for  $\langle\omega^2\rangle^{1/2}$  is quite sufficient to carry it across the barrier to **LY1**, which would then be an intermediate on the way to **W1**. This would agree with an earlier suggestion<sup>6</sup> that some intermediate structure might be present in the initial stages of the phase transition, before nucleation of **W1** sets in.

Further studies including high-temperature single-crystal NMR work are in progress on this interesting system.

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(17) The reaction paths are certainly more complicated than suggested by Figure 2, but the  $\varphi$  coordinate must represent an important component.

### Kinetics of Iron(III) Porphyrin Catalyzed Epoxidations

Teddy G. Traylor,\* James C. Marsters, Jr., Taku Nakano, and Beth E. Dunlap

Department of Chemistry D-006  
University of California, San Diego  
La Jolla, California 92093  
Received April 19, 1985

The discovery of model iron(III) porphyrin catalyzed oxidations which mimic the enzymatic epoxidation and hydroxylation reactions catalyzed by cytochrome P-450 has stimulated much interest in the kinetics and mechanisms of these model reactions.<sup>1–6</sup> These studies require stable catalysts, absence of interfering by-products, and oxidants that are soluble and highly reactive toward the catalyst but not toward the alkene. Although iron(III) tetraphenylporphyrin is rapidly destroyed during catalytic epoxidation by peracids or iodosylbenzenes,<sup>6</sup> the introduction of bulky and electronegative substituents on the phenyl rings has been shown to greatly reduce this catalyst destruction.<sup>7,8</sup> Peracids are not sufficiently reactive with iron(III) porphyrins and they react directly with alkenes.<sup>8–10</sup> Iodosylbenzene is much more reactive

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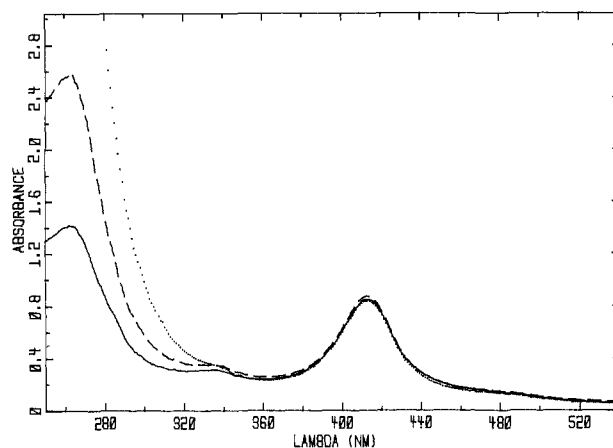
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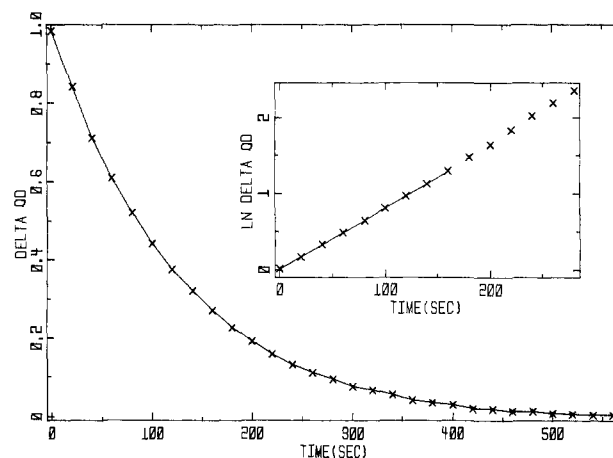
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**Figure 1.** Spectra of reactants and product solutions in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}/\text{H}_2\text{O}$  (80:18:2). (···) Computer sum of a solution  $8.9 \times 10^{-6}$  M TDCPPFeCl and a solution of 0.5 M norbornene and  $10^{-3}$  M  $\text{F}_5\text{C}_6\text{IO}$ . (—) Spectrum of a solution originally having these concentrations after a kinetic run. (---) Spectrum of the same solution after addition of a second aliquot of the  $\text{F}_5\text{C}_6\text{IO}$  to make the solution again  $10^{-3}$  M in this oxidant. The spectrum was taken after the second kinetic run. Solvent base line was subtracted from all spectra.



**Figure 2.** Plots of  $A - A_\infty$  and  $\ln(A - A_\infty)$  vs. time for a solution of  $4.2 \times 10^{-6}$  M TDCPPFeCl, 1.0 M norbornene, and  $10^{-3}$  M  $\text{F}_5\text{C}_6\text{IO}$  in  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}/\text{H}_2\text{O}$  (80:18:2) at 25 °C. Only one of every 20 points is plotted. Rate data are calculated using all points.

toward the catalysts than toward alkenes.<sup>8</sup> However, iodosylbenzenes are insoluble in methylene chloride, ketones, etc.

We wish to report oxidant systems that meet all the criteria for kinetic studies of very rapid, high turnover catalyzed epoxidation without catalyst destruction, along with preliminary kinetic results with these systems.

Pentafluoriodosylbenzene (PFIB)<sup>8,11</sup> reacts directly with only the most strained or electron-rich alkenes but reacts very rapidly with iron(III) porphyrins even in methylene chloride where it is insoluble. However, it dissolves readily in alcohols where its reactivity is reduced. Addition of water and methylene chloride increases the reaction rate. Systems we have found convenient for rapid oxidations are methylene chloride/trifluoroethanol/water (80:18:2) or methylene chloride/methanol/water (80:18:2). Concentrations of PFIB up to 0.03 M are obtainable.

In these solvent systems PFIB reacts very slowly, if at all, with alkenes but very rapidly with the catalysts as shown below.<sup>12</sup>

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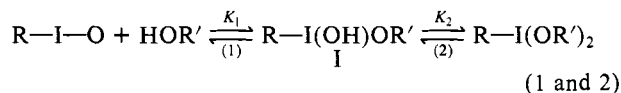
(12) In either this or the methanol solvent system, iron(III) tetraphenylporphyrin and iron(III) tetramesitylporphyrin are destroyed during the kinetic runs.

**Table I.** Kinetics of Iron(III) Porphyrin Catalyzed Epoxidations at 25 °C

catalyst R	catalyst concn, M	solvent (ratio by volume)	oxidant <sup>a</sup> concn, M	alkene <sup>b</sup> concn, M	wavelength	$k_{\text{obsd}}$ , s <sup>-1</sup>	$k_1 \times 10^{-3}$ , <sup>c</sup> M <sup>-1</sup> s <sup>-1</sup>
	$4 \times 10^{-6}$	B, 80:18:2 <sup>e</sup>	$1 \times 10^{-3}$	0.5 N	280	0.002	0.5
	$2 \times 10^{-5}$	A, 45:45:10	$4 \times 10^{-3}$	0.15 Cy	290	1.4	70
	$5 \times 10^{-7}$	A, 89:10:1 <sup>e</sup>	$1 \times 10^{-3}$	0.01 C	280	0.025	50
	$5 \times 10^{-7}$	A, 89:10:1	$1 \times 10^{-3}$	0.5 Cy	280	0.025	50
	$5 \times 10^{-7}$	A, 89:10:1	$1 \times 10^{-3}$	0.5 H	280	0.022	44
	$7 \times 10^{-7}$	A, 89:10:1	$1 \times 10^{-3}$	0.5 N	280	0.02	30
	$5 \times 10^{-7}$	A, 78:20:2	$1 \times 10^{-3}$	0.5 N	280	0.13 <sup>f</sup>	26
	$4.2 \times 10^{-6}$	B, 80:18:2	0.03	0.5 N	350	0.004 <sup>f</sup>	1.0 <sup>g</sup>
	$4.2 \times 10^{-6}$	B, 80:18:2	$1 \times 10^{-3}$	1.0 N	285	0.008	1.9
	$4.2 \times 10^{-6}$	B, 80:18:2	$1 \times 10^{-3}$	0.5 N	285	0.008	1.8
	$7.1 \times 10^{-6}$	B, 80:18:2	$1 \times 10^{-3}$	0.2 N, 0.2 C	285	0.012	1.7
	$4.2 \times 10^{-6}$	B, 80:18:2	$1 \times 10^{-3}$	0.25 N	285	0.006	1.4
	$4.2 \times 10^{-6}$	B, 80:18:2	$1 \times 10^{-3}$	0.01 N	285	0.005	1.2 <sup>g</sup>
	$4.2 \times 10^{-6}$	B, 80:18:2 <sup>h</sup>	$1 \times 10^{-3}$	0.5 H	285	0.003	0.8
	$9 \times 10^{-6}$	B, 80:18:2 <sup>h</sup>	$1 \times 10^{-3}$	0.5 Cy	285	0.018	2.2
	$9 \times 10^{-6}$	B, 80:18:2 <sup>h</sup>	$1 \times 10^{-3}$	0.5 V	285	0.018	1.9
	$5 \times 10^{-6}$	B, 80:18:2	$10^{-3}$ PhIO	0.5N	285	0.005	1.0

<sup>a</sup>The oxidant is pentafluoroiodosylbenzene unless specified otherwise. <sup>b</sup>Alkene abbreviations: N = norbornene, C = *cis*-cyclooctene, Cy = cyclohexene, H = *cis*-2-hexene, V = vinyltrimethylsilane. <sup>c</sup> $k_1 = k/[\text{catalyst}]$ . <sup>d</sup>Hemin syntheses are described elsewhere.<sup>8</sup> <sup>e</sup>The solvent A is CH<sub>2</sub>Cl<sub>2</sub>/CF<sub>3</sub>CH<sub>2</sub>OH/H<sub>2</sub>O, and B is CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH/H<sub>2</sub>O. <sup>f</sup>The first-order rate plot was somewhat curved. <sup>g</sup>The Soret band shifted to lower wavelength in these runs indicating some methanol oxidation to formic acid. <sup>h</sup>These solutions contained 0.1 M formic acid which removed an inhibition period. Norbornene oxidation is unaffected by this concentration of formic acid.

Furthermore, as in the heterogeneous reactions,<sup>8</sup> yields of epoxides are nearly quantitative and turnovers high (e.g., 10000 epoxides/catalyst). We interpret this reaction in alcohols as an addition to the iodosylbenzene to produce a "peracid-like" compound (I), in analogy to the conversion of iodosylbenzene to



dimethoxyiodobenzene reported by Schardt and Hill.<sup>3b</sup>

Fortunately, as depicted in Figure 1, the absorptions of iodobenzene in alcohols from 250 to 350 nm greatly exceed those of either the iodobenzenes or the iron(III) porphyrins, providing a very convenient method of following the kinetics, some of which require stopped-flow techniques.

Figure 2 shows plots of absorbance vs. time and  $\log(A - A_\infty)$  vs. time at 285 nm after the addition of  $4.2 \times 10^{-6}$  M iron(III) tetrakis(2,6-dichlorophenyl)porphyrin chloride to a solution of 0.001 M PFIB and 1.0 M norbornene in methylene chloride/methanol/water (80:18:2). The final spectrum and GLC analyses indicated complete conversion to the iodobenzene and the epoxides. Similar results were obtained with iodobenzene although the rates of reaction are slower. Table I summarizes kinetic data with several alkenes, solvent systems, etc.

The first-order rate constant varies with solvent composition. In 80% methylene chloride/20% trifluoroethanol the reaction is accelerated by the addition of water up to about 2% water in the solvent. This is consistent with the postulated equilibria of eq 1 and 2 and suggests that the dihydroxy derivative is not formed since iodobenzene is insoluble in water. The reaction rate is about the same in 89:10:1 methylene chloride/trifluoroethanol/water as in a 78:20:2 mixture of the same components. However, substitution of methanol for trifluoroethanol reduces the rate constant by a factor of 10.

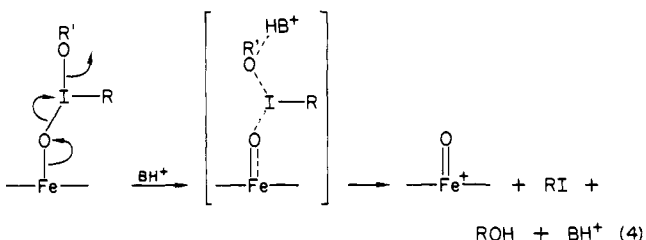
This reaction is very fast (e.g.,  $t_{1/2} = 25$  s at  $5 \times 10^{-7}$  M catalyst) and can occur with high ( $\sim 10^4$ ) turnover without catalyst destruction. Turnover rates as high as 300 (epoxides/catalyst)/s for norbornene epoxidation are easily obtained. The reaction is first order in oxidant for both iodobenzene and pentafluoroiodosylbenzene over the wide concentration range used (from  $10^{-4}$

to  $3 \times 10^{-2}$  M). It is also first order in the catalyst and essentially independent of concentration or structure of the alkene.<sup>13</sup> The second-order rate constants thus obtained are  $6 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup> in the trifluoroethanol solvent and  $2 \times 10^3$  M<sup>-1</sup> s<sup>-1</sup> in the methanol solvent using pentafluoroiodosylbenzene and iron(III) tetrakis(2,6-dichlorophenyl)porphyrin.<sup>14</sup> The kinetics of these reactions under our conditions are described in eq 1.

$$\frac{d(\text{epoxide})}{dt} = \frac{-d(\text{RIO})}{dt} = k_1(\text{Hm}^+)(\text{RIO}) \quad (3)$$

Although solvent effects and preliminary studies of general-acid catalysis suggest a more complex form of eq 3, it is not yet possible to express the rate as a function of other concentrations.

It is interesting that the rates of reaction of pentafluoroiodosylbenzene and iodobenzene differ by less than a factor of 2 in solution in contrast to the two-phase reactions in methylene chloride where the former reacts much faster than does iodobenzene.<sup>8</sup> These results and the solvent effect of rate suggest that the driving force is in the stability of the R'O<sup>-</sup> leaving group rather than the iodobenzene.

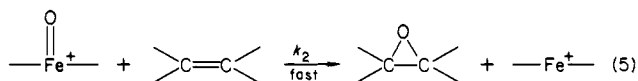


As in the case of hemin-catalyzed phenol oxidation,<sup>9</sup> these kinetics do not provide evidence concerning the mechanism of

(13) In the absence of substrate, methanol is oxidized more slowly than are alkenes even though hemin is not destroyed. Thus, high-valent iron intermediates do seem to accumulate and alkene dependence should appear under some conditions.

(14) These rapid rates can be contrasted to a bimolecular rate constant for the reaction of iron(III) tetraphenylporphyrin and iodobenzene in pure ethanol of about 1 M<sup>-1</sup> s<sup>-1</sup> reported by Shannon and Bruice.<sup>4b</sup> Clearly, water has a large effect on the rate.

oxygen transfer to the alkene except to show that intermediates are extremely unstable, making reaction 5 much faster than reaction 4.



The discovery of a homogeneous, rapid, and high-turnover catalytic epoxidation system, whose kinetics are easily followed, provides a means of determining detailed mechanisms of this reaction as well as that of catalyzed hydroxylation.<sup>13</sup> The nature of the iodosylbenzene species in solution and the nature of their reactions with metalloporphyrins are under study.

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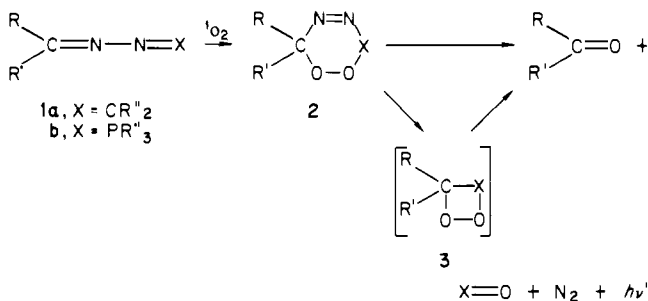
### Oxidation of Phosphazine by Singlet Oxygen. High-Field <sup>31</sup>P NMR Spectroscopic Studies of 3-Phospha-1,2-dioxa-4,5-diazine and Phospha-1,2-dioxetane

Takeshi Akasaka, Rikiya Sato, and Wataru Ando\*

Department of Chemistry, University of Tsukuba  
Sakura-mura, Ibaraki 305, Japan

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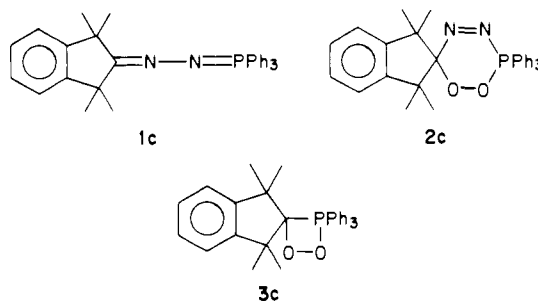
Extensive studies have been focused on the reaction of singlet oxygen with conjugated dienes, and the simplest view of this reaction as a concerted [2 + 4] cycloaddition is widely accepted.<sup>1-3</sup> Meanwhile, only little attention has been drawn to photooxygenation of azines (1a),<sup>4-8</sup> nitrogen analogues of acyclic conjugated dienes, and phosphazines (1b)<sup>9</sup> in connection with chemiluminescent systems.<sup>10</sup> Lechtken reported the formation of acetone from the direct decomposition of 1,2-dioxa-4,5-diazine (2a) formed by the photooxygenation of acetone azine and observed the chemiluminescence of the products.<sup>5</sup> Suzuki et al. also described a similar type of photooxygenation of benzophenone and fluorenone triphenylphosphazine, which forms 3-phospha-1,2-dioxa-4,5-diazine (2b) and phospha-1,2-dioxetane (3b) as intermediates, and the chemiluminescence of the products.<sup>9</sup>



Meanwhile, Landis proposed a free-radical pathway initiated by singlet oxygen to give a linear peroxide polymer.<sup>7</sup> No direct evidence for the formation of 1,2-dioxa-4,5-diazine 2, however, was revealed at all. We wish to present here the first direct observation of 3-phospha-1,2-dioxa-4,5-diazine (2b) and its thermal decomposition product, phospha-1,2-dioxetane (3b) by high-field <sup>31</sup>P NMR spectroscopy.<sup>11</sup>

Photooxygenation of 1,1,3,3-tetramethyl-2-indanone triphenylphosphazine (1c)<sup>12</sup> at 15 °C afforded the corresponding ketone and triphenylphosphine oxide as major products accompanied with a small amount of 2,2,5,5-tetramethyl-3,4-benzo-3-penten-5-olide. A strong light emission was also observed when the reaction was carried out at -78 °C and then warmed to room temperature.<sup>13</sup> These findings encouraged us to carry out an exploratory experiment to observe the suspected intermediates.

A tetrahydrofuran solution (2 mL) of phosphazine 1c (1.4 × 10<sup>-1</sup> M) with polymer-bound rose bengal<sup>14</sup> as a sensitizer was irradiated at -100 °C for 3 h with bubbling oxygen with two 500-W halogen lamps. A characteristic feature of the suspected intermediate, diazine 2c, is seen in the <sup>31</sup>P NMR spectrum (-100 °C). Two resolved singlets appeared at -44.3 and -47.1 ppm in a ratio of 1:1, respectively, together with two other singlets at 25.8 (triphenylphosphine oxide) and 15.1 ppm (unreacted 1c). The



course of the decomposition of 2c was monitored with temperature. No change was observed in the spectrum between -100 and -90 °C. When the sample was warmed to -80 °C, the diazine peaks decreased and a new singlet arose at -53.4 ppm presumably due to the formation of dioxetane 3c. At -70 °C, the diazine peaks completely disappeared and the dioxetane peak still remained. Finally, all transient peaks in the spectrum disappeared at 27 °C.

Two important results are evident for these experiments. That the <sup>31</sup>P NMR spectrum revealed pairs of singlets between -44 and -48 ppm might be best explained by intramolecular ligand reorganization; i.e., pseudorotation between two conformers (2c' and 2c'') of diazine 2c.<sup>15-17</sup> Pseudorotation using the azo group as pivot may easily take place. At low temperature, however, the pseudorotation process becomes slow and the separate signals might represent 2c' and 2c''.<sup>18</sup> Diazine 2c undergoes thermal

(11) High-field <sup>31</sup>P NMR spectra were recorded by a JMN(JEOL) JX-400 NMR spectrometer at 161.8 MHz (broad-band proton decoupling) in 10 mm diameter NMR tube in tetrahydrofuran using phosphoric acid as an internal standard.

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(17) It could not be assigned without further study which of these peaks was due to 2c' or 2c''.

(18) 2c decomposed before coalescence temperature. An approximate value of *k<sub>c</sub>*, the rate constant at coalescence, may be calculated from the expression, *k<sub>c</sub>* = πΔν/2<sup>1/2</sup>, where Δν is the maximum chemical shift difference (in hertz) between the separate signals; hence, in this case, *k<sub>c</sub>* = π × 464/2<sup>1/2</sup> = 1 × 10<sup>3</sup> s<sup>-1</sup>.<sup>16b</sup>

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