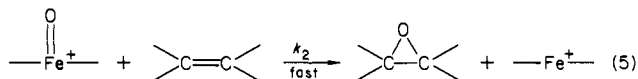


oxygen transfer to the alkene except to show that intermediates are extremely unstable, making reaction 5 much faster than reaction 4.



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.¹³ The nature of the iododibenzene species in solution and the nature of their reactions with metalloporphyrins are under study.

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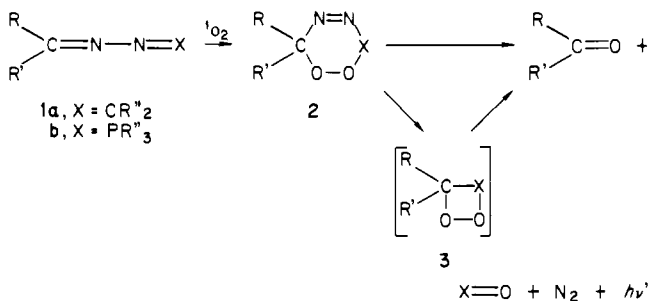
Oxidation of Phosphazine by Singlet Oxygen. High-Field ³¹P NMR Spectroscopic Studies of 3-Phospha-1,2-dioxa-4,5-diazine and Phospha-1,2-dioxetane

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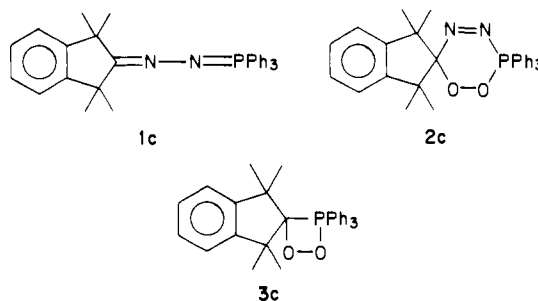
Extensive studies have been focused on the reaction of singlet oxygen with conjugated dienes, and the simplest view of this reaction as a concerted [2 + 4] cycloaddition is widely accepted.¹⁻³ Meanwhile, only little attention has been drawn to photooxygenation of azines (**1a**),⁴⁻⁸ nitrogen analogues of acyclic conjugated dienes, and phosphazines (**1b**)⁹ in connection with chemiluminescent systems.¹⁰ 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.⁵ 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.⁹



Meanwhile, Landis proposed a free-radical pathway initiated by singlet oxygen to give a linear peroxide polymer.⁷ 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 ³¹P NMR spectroscopy.¹¹

Photooxygenation of 1,1,3,3-tetramethyl-2-indanone triphenylphosphazine (**1c**)¹² 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.¹³ 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 × 10⁻¹ M) with polymer-bound rose bengal¹⁴ 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 ³¹P 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 ³¹P 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**.¹⁵⁻¹⁷ 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''**.¹⁸ Diazine **2c** undergoes thermal

(11) High-field ³¹P 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_c*, the rate constant at coalescence, may be calculated from the expression, *k_c* = πΔν/2^{1/2}, where Δν is the maximum chemical shift difference (in hertz) between the separate signals; hence, in this case, *k_c* = π × 464/2^{1/2} = 1 × 10³ s⁻¹.^{16b}

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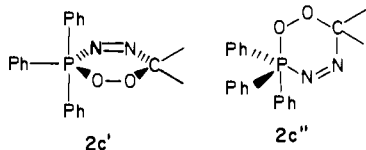
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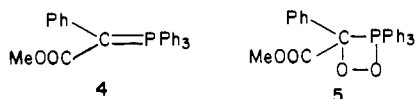
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decomposition to form dioxetane **3c** as second intermediate by loss of nitrogen.⁹ At -80 °C, however, the pseudorotation in **3c** occurs within the time scale of the NMR experiment. This phosphadioxetane might be responsible for the chemiluminescence similar to the case of dioxetanes.¹⁹

Parallel ^{31}P NMR studies were carried out for the direct observation of phosphadioxetane which could be derived from photooxygenation of phosphonium ylides.²⁰ The reaction mixture of photooxygenation of $[\alpha\text{-(methoxycarbonyl)benzylidene}]$ triphenylphosphorane²¹ (**4**, 2.4×10^{-1} M) gave a ^{31}P NMR spectrum (-107 °C) featuring pairs of singlets at -25.8 and -26.9 ppm in a ratio of 0.9:1, respectively, together with two other singlets: 25.8 (triphenylphosphine oxide) and 20.8 ppm (unreacted **4**). On



warming to 27 °C, both upfield peaks disappeared. We can assign such upfield peaks as those of the conformers of dioxetane **5**^{16,23,24} similar to the case of diazine **2c**.

Acknowledgment. We thank Y. Nagai, Eisai Company Co., Ltd., for measurement of the high-field ^{31}P NMR spectra.

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(24) An approximate value of k_c is $4 \times 10^2 \text{ s}^{-1}$.^{16b}

Phase Transitions Affecting Intramolecular Electron Transfer in Mixed-Valence Trinuclear Iron Acetate Complexes¹

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In a recent paper³ we suggested that in the solid state the ability of one of the three 4-ethylpyridine ligands of oxo-centered $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6(4\text{-Et-py})_3](4\text{-Et-py})$ to move between two positions as the temperature of the crystal was increased controlled

(1) A part of this paper corresponds to Contribution No. 89 from the Chemical Thermodynamics Laboratory.

(2) On sabbatical leave from the Department of Engineering Physics, The University of Electro-Communications, Tokyo, Japan.

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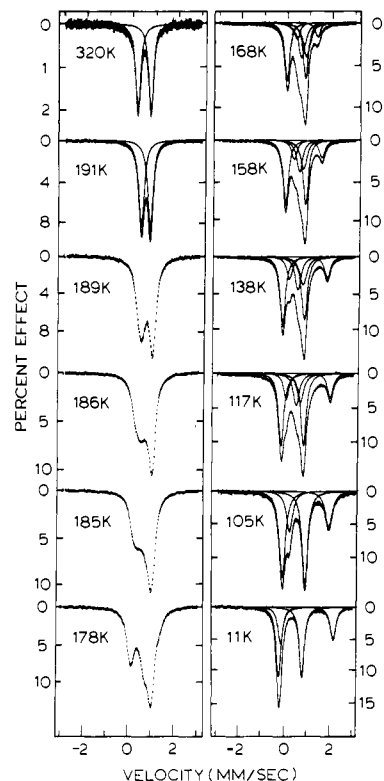


Figure 1. Variable-temperature ^{57}Fe Mössbauer spectra for $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{py})_3](\text{py})$. Velocity scale is referenced to iron foil at room temperature.

the rate of intramolecular electron transfer in the mixed-valence Fe_3O complex. In this paper direct evidence will be presented for the presence of phase transitions in $[\text{Fe}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{py})_3](\text{py})$ (**1**) that affect the rate of intramolecular electron transfer.

Compound **1** is isostructural with the analogous manganese complex.^{4,5} In the room-temperature space group $R\bar{3}2$ the Fe_3O triangular complexes are arranged in stacks with C_3 axes oriented down the stacks. Ongoing single-crystal X-ray work⁶ shows that the pyridine solvate molecules are sandwiched between the Fe_3O complexes in the stacks. The plane of the solvate molecule is perpendicular to the Fe_3O plane. At room temperature the pyridine solvate molecules are disordered in three positions about the C_3 axis.

Variable-temperature Mössbauer spectra for **1** are shown in Figure 1. At temperatures below ~ 100 K, two quadrupole-split doublets are seen, one characteristic of high-spin Fe^{II} and the other of high-spin Fe^{III} . As the sample temperature is increased from 11 K, the first appreciable change in the spectrum is seen at ~ 117 K, where a third doublet appears. The spectrum changes dramatically as the temperature is further increased, eventually to become a single average doublet⁷ at temperatures above ~ 190 K. It is clear that the rate of intramolecular electron transfer is increasing with increasing temperature. Above ~ 190 K it exceeds the $\sim 10^7$ – 10^8 s^{-1} rate which the Mössbauer technique can sense.

The heat capacity at constant pressure was measured for a 17.7794-g sample of **1** from 12 to 300 K. As can be seen in Figure 2, there are basically two phase transitions present, a first-order

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