predicted by Chipman and Miller (Table I, Column A). The large value of a_3 is similar to that observed for the corresponding protons in 1,2-dimethylcyclopropen-3-yl[4b] and is characteristic for a σ radical. This requires that the hydrogen is substantially bent out of the ring plane, probably by 40–50°.

Our present work does not enable us to determine the dynamics of pseudorotation in **1a** because the matrix softens at 140 K and the spectrum disappears. However, there are no substantial changes on heating from 20 to 140 K, putting a lower limit of 3 kcal/mol on the height of the barrier if we assume the preexponential factor to be $10^{12.5}$–10^{13}.

In summary, we believe we have generated and trapped the elusive cyclopropen-3-yl radical and have determined its symmetry and gross structure. Perhaps the most remarkable outcome of this work is the almost quantitative agreement of the observed EPR spectrum with the predicted one, demonstrating the power of modern ab initio MO methods!

Acknowledgment. We are grateful to C. Lin for assistance in the experiments and to J. R. Norris for advice on the simulations.

Registry No. 1, 19469-08-0; 3-chlorocyclopropene, 17336-56-0.

On the Mechanism of Olefin Epoxidation by Oxo–Iron Porphyrins. Direct Observation of an Intermediate

John T. Groves* and Yoshihito Watanabe

Department of Chemistry, The University of Michigan
Ann Arbor, Michigan 48109

Received August 5, 1985

Interest in the elucidation of biological strategies for the metabolism of oxygen has focused sustained attention on the mechanism of cytochrome P-450[1] and the development of synthetic metalloporphyrin models[2] for these processes. That an oxo-iron intermediate is produced in the enzymic cycle is now generally accepted.[3] Rate saturation and competitive inhibition for iron and manganese porphyrin systems have been interpreted by Collman et al. to indicate the formation of a stable intermediate during the epoxidation of olefins.[2m,n] The preparation and characterization of an oxo–iron(IV) porphyrin radical species, **1**, in our laboratories[4] which is kinetically competent to oxidize hydrocarbons has now allowed the examination of the oxygen-transfer step. We describe here the direct observation of an intermediate olefin–iron porphyrin complex and its subsequent evolution to the product epoxide.

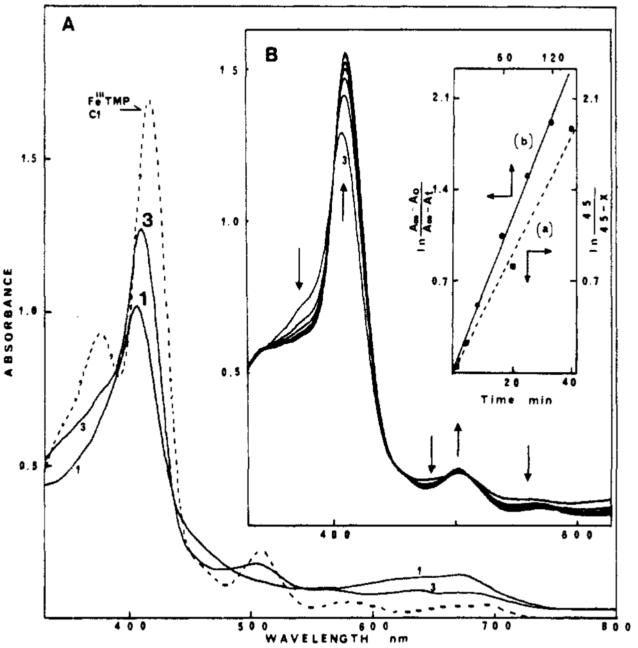

Figure 1. (A) (- - -) Based on yields of cyclooctene oxide (A^∞ = 45%) at −78 °C in 430 μL of CH_2Cl_2 containing Fe(TMP)Cl (3.9 × 10^{-3} mmol), mCPBA (4.3 × 10^{-3} mmol), and cyclooctene (3.1 × 10^{-2} mmol). (B) (—) Based on the spectral change from **3** to Fe^{III}TMP at 416 nm in CH_2Cl_2 at −43 °C.

Visible spectral changes after the addition of olefins to **1** *indicated that a stable intermediate was formed prior to epoxide production.* The oxidation of either Fe(TMP)Cl or Fe(TMP)OH (**2**) (TMP = 5,10,15,20-tetramesitylporphyrin) (1.63 × 10^{-5}M) in methylene chloride with 2.2. equiv of *m*-chloroperoxybenzoic acid (mCPBA) at −42 °C produced a visible spectrum characteristic of **1** (Figure 1A). The addition of 5 μL of cyclooctene caused a distinct color change, green to dark green, within a minute, and an altered visible spectrum (Figure 1A) of an intermediate species **3** appeared which decayed in a first-order fashion over 3 h to Fe^{III}(TMP) (Figures 1B and inset b; k = 2.8 × 10^{-4} s^{-1}). The EPR spectrum of this intermediate (**3**) formed at −78 °C with 1.1 equiv of mCPBA followed by 8 equiv of cyclooctene showed no evidence of iron(III) but **3** decomposed to Fe^{III}(TMP) upon warming to room temperature.

Quenching **3** with iodide after 24 s gave less than 2% cyclooctene oxide. Lengthening the time between olefin addition and the iodide quench caused a *first*-order increase in the epoxide yield over 5 h to a maximum of 45% at a rate similar to the appearance of iron(III) (k = 3.2 × 10^{-4} s^{-1}) (Figure 1B, inset a). However, the addition of 3 equiv of imidazole or 1% methanol to a preformed solution of **3** at −78 °C led to a 46% yield of cyclooctene oxide after only 3 min.

The rate of reaction of **1** *with substituted styrenes correlated with the Hammett* σ^+. Fe(TMP)OH (**2**) was oxidized in methylene chloride with 2.2 equiv of mCPBA at −50 °C to produce **1**. Upon the addition of 400–2000 equiv of styrene both the disappearance of **1** and the formation of **3** were monitored over at least 2 half-lives (40–200 s). Good pseudo-first-order kinetics were obtained for all substrates and no rate saturation was observed under these conditions. The observed rate constants correlated with σ^+ with a large negative ρ^+ (−1.9). The reaction of **1** with the same styrenes in the presence of 1% methanol led to the regeneration of Fe^{III}TMP with the identical Hammett correlation (x = *p*-OMe, *p*-Me, H, *p*-Cl).

The adduct **3** *formed from* **1** *and cyclooctene decomposed in the presence of methanol and styrene to produce only cyclooctene oxide.* A 1-mL solution of **1** formed at −78 °C from Fe^{III}(TMP)Cl (7.8 × 10^{-3} M) and 1.2 equiv of mCPBA in methylene chloride was allowed to react with 10 μL of cyclooctene for 5 min to product **3**. The addition of 10 μL of styrene led to the *slow* production of cyclooctene oxide (37%) and styrene oxide (17%)

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* Current Address: Department of Chemistry, Princeton University, Princeton, NJ 08544.

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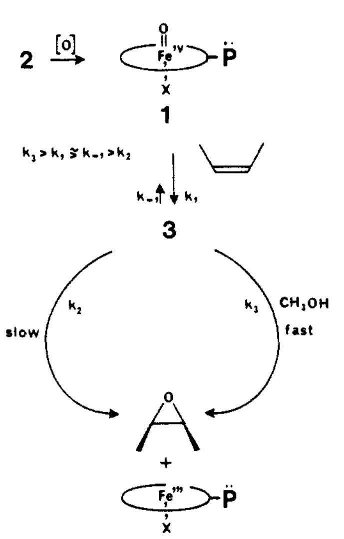
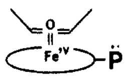
Scheme I





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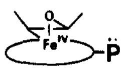

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after 4 h. When 50 μL of methanol containing 10 μL of styrene was added to an identical solution of 3 at −78 °C, 41% of cyclooctene oxide and *no styrene oxide* were detected after 10 min.

These results show unambiguously that an intermediate, 3, was formed rapidly upon the addition of olefins to 1 and that the rate of its formation was sensitive to the concentration and structure of the olefin. In the absence of imidazole or methanol, 3 decomposed slowly to Fe^{III}TMP and epoxide. The isolation of styrene oxide upon addition of styrene to 3 suggests that the formation of 3 was *reversible* under these conditions, consistent with the recent kinetic analysis of Collman et al.[2m,n] The very rapid evolution of epoxide in the presence of methanol or imidazole and the production of *only* cyclooctene oxide when 3 was quenched with methanol–styrene indicates that the conversion of 3 to cyclooctene oxide was faster in the presence of methanol than its reversion to 1. Accordingly, *the formation of 3 must be rate-limiting as well as product-determining in the presence of methanol.* The similarity of the Hammett plots for the formation of 3 in the absence of methanol and the formation of Fe(III)TMP in the presence of methanol confirms this interpretation.

A mechanism for oxygen transfer from 1 to olefins via an intermediate 3 consist with these observations is presented in Scheme I. The negative Hammett ρ^+ is consistent with an initial electron-transfer process[5] between 1 and the substrate as proposed by Ortiz de Montellano[6] and by Watanabe[7] for cyclochrome P-450. Two likely possibilities for the structure of the intermediate 3 are an olefin π-complex (4) and an oxametallacycle (5).[2m,n,8] The dark green color of 3, the characteristic visible spectrum,[9] and the weak EPR spectrum indicate a porphyrin radical similar to 1.[10] That the reductive quenching of 3 with iodide decreased the amount of product indicates that the product epoxide was not fully formed at this stage. The profound effect of added imidazole or methanol on the rate of conversion of 3 to Fe^{III}TMP and epoxide suggests an important role for axial coordination of the iron on the kinetics of epoxide release.[11] A detailed examination of 3 and its reactions is under way.

Acknowledgment. Support for this research by the National Institutes of Health (GM 25923) is gratefully acknowledged. We thank Professor T. G. Traylor for an insightful discussion regarding the trapping of 3.

Note Added in Proof. The ^{1}H NMR spectrum of 3 was typical of a porphyrin cation radical but lacking the high-field resonance of 1.

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Methylene-Carbonyl Coupling: Formation of Bridging η^3-Ketene and η^4-Oxaallyl Complexes

Jennifer S. Holmgren, John R. Shapley,* Scott R. Wilson, and William T. Pennington

School of Chemical Sciences, University of Illinois
Urbana, Illinois 61801

Received September 23, 1985

Formation of C–C bonds via insertion of CO into M–CH$_2$ is a fundamental reaction type of potential relevant to both stoichiometric[1] and catalytic[2] transformations mediated by transition metals. In previous examples involving formation of ketene ligands, further reaction of these ketenes has been limited to elimination of methyl acetate and related organics.[1d,f,g] It has, therefore, been assumed that CO insertion into M–CH$_2$ leads only to C$_2$-oxygenated products. We wish to report the synthesis and characterization of two unique ruthenium complexes, the first, which contains both a methylene ligand and an O-bound ketene ligand, and the second, which is generated by carbon monoxide induced coupling to these ligands to form a bridging η^4-oxaallyl moiety.

Treatment of Ru$_3$(CO)$_{10}$(dppm)[3] (1) with 2–3 equiv of ethereal diazomethane in refluxing toluene for 10 min provides a mixture of unreacted 1 (25–30%), the ligand cleavage product Ru$_3$(CO)$_9$[μ-P(C$_6$H$_5$)CH$_2$P(C$_6$H$_5$)(C$_6$H$_4$)][4] (5–10%), and a new complex characterized as Ru$_3$(CO)$_7$(μ_3,η^3-C(O)CH$_2$)(μ-CH$_2$)(dppm) (2). Evaporation, TLC separation, and crystallization from pentane–acetone gave 2·CH$_3$COCH$_3$ in 30% yield as red-orange crystals.[5]

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